





Article

Grafting of Cellulose and Microcrystalline Cellulose with Oligo(*L*-lactic acid) by Polycondensation Reaction

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Abstract: Oligo(*L*-lactic acid) (OLLA) was synthesized by ring opening polymerization of *L*-lactides using stannous octoate (0.03 wt% of lactide). While this served as the initiator, *L*-lactic acids were the co-initiators at 140 °C for 10 h, wherein *L*-lactic acids were prepared by hydrolytic degradation of *L*-lactides at 100 °C for 1 h. The molecular weight or degree of polymerization was controlled with monomer/co-initiator ratio (mol/mol). α -cellulose and microcrystalline cellulose (MCC) were extracted from jute fiber by subsequent treatment with sodium chlorite (Na₂ClO₂), NaOH and H₂SO₄. Grafting of OLLA onto α -cellulose and MCC in toluene was carried out using para-toluene sulphonic acid as a catalyst and potassium persulphate (KPS) as an initiator at 130 °C under 380 mm (Hg) pressure for 3, 6, 9, 12, 15, and 18 h. New properties of α -cellulose and MCC were observed due to the successful grafting onto α -cellulose and MCC. Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) were conducted in order to confirm grafting of OLLA onto cellulose and MCC. The FTIR analysis results showed there are some new characteristic absorption peaks appeared (1728 to 1732 cm⁻¹) in the spectrum, which confirmed the grafting of OLLA onto α -cellulose and MCC was successful. SEM images of α -cellulose and MCC before and after grafting revealed significant changes in surface morphology. Grafting of MCC could be more effective for further application in comparison to α -cellulose.

Keywords: grafting; polycondensation; oligo(*L*-lactic acid); cellulose; microcrystalline cellulose



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1. Introduction

Cellulose is the main constituent of plants and one of the most abundant natural polymers. It has attracted great attention for its potential for various applications including as a reinforcing agent in polymeric composites, biodegradable adsorbent, and biomedical agent due to its low cost, high mechanical strength, and biodegradability [1–5]. Furthermore, it can increase composite stiffness and structural strength through hydrogen bond formation between different hydroxyl groups [6]. It has also been reported that microcrystalline cellulose (MCC) improves thermosetting polymers' mechanical and thermal properties [7–12]. However, hydroxyl groups derived from cellulose/MCC produce some hydrogen interaction between two fibrils that produce a gel-like structure affecting the homogeneous dispersion of hydrophilic cellulose in the hydrophobic polymer matrix. This can also be an obstacle when searching for better interfacial adhesion between the components of the final composites [13]. Therefore, physical or chemical modification of " α -cellulose

and MCC" is necessary to enhance the compatibility between α -cellulose/MCC and the polymer matrix [12,14].

Several chemical surface modification methods including ring-opening polymerization (ROP), atom transfer radical polymerization, reversible addition-fragmentation chain transfer, nitroxide-mediated polymerization, and single-electron transfer-living radical polymerization have been used to modify cellulose surfaces [15,16]. Some polymer chains have been covalently bonded onto the cellulose surface using these methods, which markedly changed the surface performance [17,18]. Grafting is a versatile method to produce new block or graft copolymers. Graft copolymers of poly(*L*-lactic acid) (PLLA) have been synthesized with monomer/polymers such as chitosan, cellulose, starch, lignin, dextran, methyl methacrylate, maleic anhydride, and graphene oxide [19]. The influence of different contents of MCC on the mechanical properties of PLA/MCC composites was evaluated by Xian et al. [20]. The results showed that the tensile strength of composites increased at first and then decreased with the increase in MCC content. PLLA also could be used for grafting on to the surface of cellulose and MCC to improve the compatibility prior to the composite preparation. However, it is pretty challenging to form a bond between a smaller hydrophilic molecule such as PLLA and α -cellulose. On the other hand, low molecular weight polymers (oligomers) can be easily grafted onto the surface of the cellulose by ring-opening [21] or polycondensation method [12] due to their low molecular weight.

The ROP is a recognized technique to polymerize cyclic monomers such as lactones, lactams, dilactones, cyclic carbonates, cyclic ethers, oxazolines, and lactides [21–24]. The ROP of cyclic monomers such as caprolactone and lactide were carried out onto filter paper using tin(II) 2-ethylhexanoate [Sn(Oct)₂] as a catalyst [21]. Grafting of cellulose can be initiated by hydroxyl groups utilizing ROP of cyclic monomers for the grafting or modifications of cellulose or cellulose derivatives [21,25]. No chemical treatment of the cellulose is required prior to the grafting reaction compared to other polymerization methods when performed ROP from cellulose [21,26]. Grafting of cellulose fibers with caprolactone and *L*-lactide using ROP were performed by Lönnberg et al. which was aimed to increase the amount of grafting polymer on the fibers [27]. The results of their study showed an improved grafting efficiency after activation of the cellulose surface with 2,2-bis(methylol) propionic acid, where the amount of grafted polymer was controlled by the initiator (hydroxyl groups itself acted as initiator) to monomer ratios.

Methacrylic acid-MCC/PLLA composites were synthesized via grafting polymerization to obtain better compatibility and increasing the tensile strength of PLA composites [28,29]. Novel ethyl cellulose-graft-poly (caprolactone)-block-poly (*L*-lactide) graft-block copolymers were synthesized via ROP of *L*-lactide using Sn(Oct)₂ as a catalyst [30]. The graft copolymer cellulose diacetate-graft-poly-(methyl methacrylate) and ethyl cellulose-graft-polystyrene/poly-(methyl methacrylate) by atom transfer radical polymerization were also reported by past studies [31,32]. Hafren and Cordova synthesized the poly-caprolactone by ROP with solid cotton and paper cellulose initiator and organic acid catalyst [26]. However, the effects of cellulose sizes (nano, micro, etc.) on the grafting reaction is still unexplored. To the best of our knowledge, grafting of MCC with oligo(*L*-lactic acid) (OLLA) by polycondensation reaction has not been reported.

In addition, in this current research, grafting onto α -cellulose and MCC with paratoluene sulphonic acid as a catalyst and potassium per sulfate as an initiator was performed for more control on polymerization reaction and to understand more about the grafting reaction.

This study aims to develop a suitable method to graft modification of MCC and α -cellulose with OLLA by polycondensation reaction in a toluene medium. Fourier-transform infrared spectroscopy (FTIR) and SEM analysis of grafted and non-grafted cellulose and MCC were carried out to evaluate the grafting reaction. Crystalline structures of the grafted cellulose and MCC were investigated by wide angle X-ray diffractometer (WAXD).

2. Materials and Methods

2.1. Materials

A sample of jute fiber was collected from the local market in the Kushtia district, Bangladesh, and L-lactide (assay 99.5%) was purchased from Purac Biochem, Gorinchem, The Netherlands. Other chemicals employed in the experiments were NaOH, ethanol from Merck, Darmstadt, Germany and NaClO₂, H₂SO₄, monochloroacetic acid, acetic acid from BDH, England. All chemicals were laboratory grade chemicals.

2.2. Synthesis of OLLA

Low molecular weight PLLA (i.e., OLLA with calculated molecular weight) was synthesized by ring opening polymerization of L-lactides in the presence of stannous octoate (0.03 wt% of lactide) as the initiator and L-lactic acid as co-initiators at 140 °C for 10 h [33] as shown in Figure 1. L-lactic acids were prepared by hydrolytic degradation of L-lactides at 100 °C for 1 h. Molecular weight or degree of polymerization was controlled with monomer/co-initiator ratio (mol/mol). The purification was not carried out for this synthesized OLLA since low molecular weight PLLA is soluble in methanol.

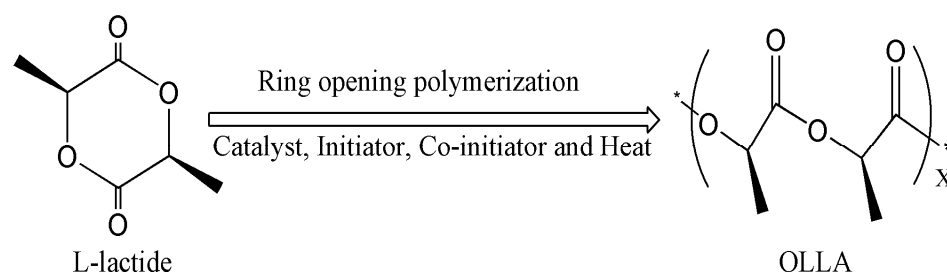


Figure 1. Synthesis of oligomer (low molecular weight PLLA).

2.3. Preparation of α -Cellulose from Jute Fiber

The α -cellulose was extracted from jute fibers. Removal of impurities of the fibers such as dirty materials and gummy substances were carried out by utilizing a solution containing 6.5 g of soap flake and 3.5 g of surfactant per liter of solution for 1 h in a beaker maintaining fiber to solution ratio 1:50. The fiber was then thoroughly washed with distilled water and dried in the oven at 105 °C. The fiber was bleached with 0.7% sodium chlorite (NaClO₂) buffer solution at constant pH 4 for 2 h at 90–95 °C to remove maximum lignin content, following by filtration and washing thoroughly with distilled water. Subsequently, the fiber was dried at 105 °C for two hours. The bleached jute fiber was then soaked in a 17.5% NaOH to reduce β - and γ -cellulose [34]. The ratio of fiber and solution was 1:25. The α -cellulose was then washed several times with distilled water and acetic acid alternatively to remove any NaOH stuck with the fiber. Then the cleaned fiber was dried in an oven at 105 °C and stored in a desiccator [35]. Bleaching with NaClO₂ and treatment with NaOH will increase the percentages of α -cellulose and may contain little amount of lignin and hemicellulose which may have negligible or no effect on grafting reaction.

2.4. Preparation of MCC

MCC was prepared from α -cellulose by the well-known acid hydrolysis process. Higher than 63 wt% of H₂SO₄ can diffuse into the α -cellulose fiber and break down glycoside bonds of the cellulose polymeric chain [36]. As prepared α -cellulose was treated with 64 wt% of H₂SO₄ solution (optimized by a number of researchers for preparation of MCC) at 35–40 °C for 25–30 min with constant stirring. The ratio between α -cellulose and 64 wt% H₂SO₄ solution was 1 g: 10 mL. After dissolving α -cellulose in acid solution, it was quenched with ice cool de-ionized water immediately to produce gel-type MCC and washed with water several times to remove acid completely, and H₂O was replaced by acetone with centrifugation [37–40]. It is insoluble in water, ethanol, ether, and dilute mineral acids.

2.5. Grafting of OLLA onto MCC and α -Cellulose

Figure 2 shows the structural representation of grafting of cellulose/MCC. About 1 g α -cellulose or MCC and 100 mL toluene was put into a three-necked round bottom reaction flask (Pyrex). The flask was equipped with a water condenser packed by four Å molecular sieves, vacuum pump, thermocouple, and a magnetic bar for stirring. The flask was kept in a temperature control oil bath. The hydroxyl groups (–OH) on the cellulose surface act as initiators for the polymerization with OLLA (100 wt% to α -cellulose) in the presence of para-toluene sulphonic acid (5 wt% to α -cellulose) and potassium persulfate (0.5 wt% to α -cellulose) for more control on polymerization [41]. The flask was sealed with Teflon and the reaction continued for 3, 6, 9, 15, and 18 h at 130 °C under 380 mm (Hg) and kept overnight at room temperature. OLLA grafted α -cellulose or MCC was soaked in acetone and stirred for 24 h to remove non-grafted polymers or oligomers. Grafted fibers were refluxed 10 times with chloroform, 3 times with acetone to remove unreacted α -cellulose or MCC, and then dried in a vacuum oven at 60 °C for 4 h. About 15–20 mL of chloroform/acetone was used per process. Then they were subjected to characterization [42]. The percentages of the grafting were calculated by the following Equation (1):

$$\text{Percentage of grafting} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_2 and W_1 represent the weight of the grafted α -cellulose and the weight of the α -cellulose, respectively.

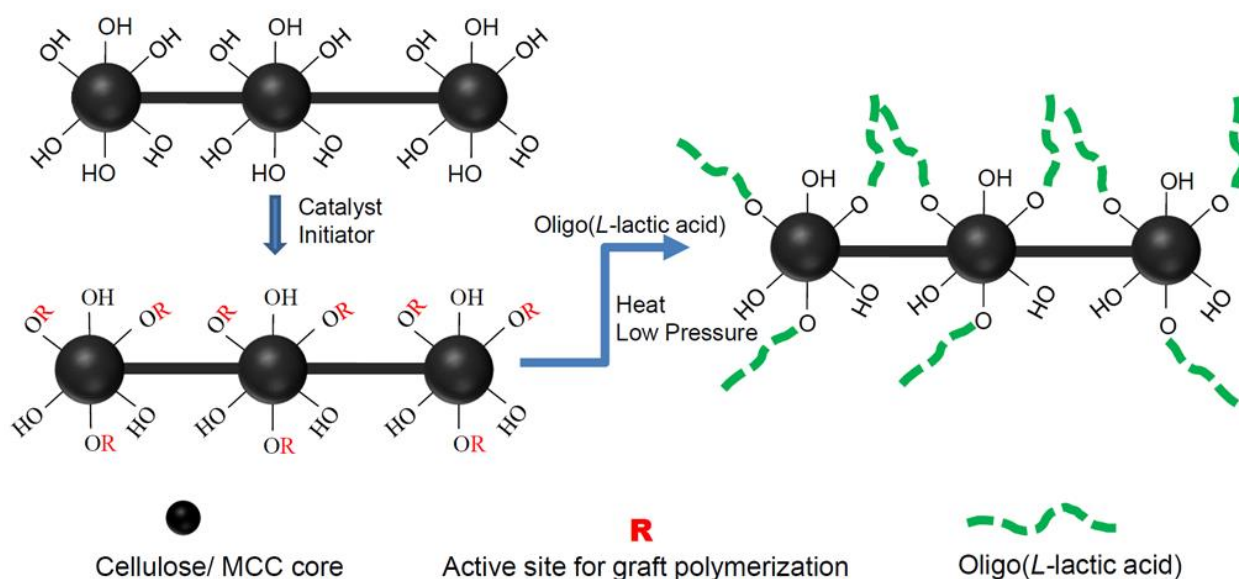


Figure 2. Structural representation of grafting of α -cellulose or MCC with oligo (*L*-lactic acid).

2.6. Measurements

The M_w and M_n of the OLLA were evaluated in chloroform at 40 °C using a Tosoh (Tokyo, Japan) GPC system (refractive-index detector: RI-8020) with two TSK gel columns (GMH_{XL}) and polystyrene standards. The FTIR (Shimadzu IR Prestige-21, Japan) were used to determine the surface functional groups onto the non-grafted and grafted α -cellulose and MCC. The surface morphologies of cellulose and MCC before and after grafting were investigated by SEM (SEM Leica AS-360FE), at various magnification ranges, which contained Tungsten (W) filament with accelerating voltage of 20 kV. The wide-angle X-ray scattering (WAXS) patterns of non-grafted, grafted α -cellulose and MCC were measured with a BRUKER D8 Advance WAXD. This involved Cu K α radiation (0.154 nm) voltage of

50 kV and current of 40 mA with 2θ ranges from 5 to 50. The crystallinity (X_c) values were estimated from the WAXS profiles using the following Equation (2):

$$X_c (\%) = 100 I_{cr} / (I_{cr} + I_{non-cr}) \quad (2)$$

where I_{cr} and I_{non-cr} are crystalline and amorphous diffraction peak areas.

3. Results and Discussion

3.1. Synthesis of OLLA

Molecular characteristics of synthesized OLLAs were shown in Table 1. Based on what can be seen in Table 1, the molecular weight distributions of synthesized OLLAs are too high. This supports the reported results for low molecular weight PLLA synthesis [43]. As the molecular weight is very low, it could not be possible to purify synthesized OLLA with methanol. These synthesized OLLAs could be used for grafting and we have used OLLA of $M_n 2.0 \times 10^2 \text{ g}\cdot\text{mol}^{-1}$ maintaining monomer/co-initiator ratio 7 for grafting of α -cellulose and MCC.

Table 1. Molecular characteristics of synthesized OLLA.

Code	Monomer/Co-Initiator	M_n [g·mol ⁻¹]	M_w/M_n
L5	5	1.8×10^2	4.2
L7	7	2.0×10^2	4.5
L9	9	2.6×10^2	5.6

3.2. Grafting

The grafting reaction of α -cellulose and MCC with OLLA continued for 3–18 h at 130 °C under 380 mmHg pressures. The percentages of the grafting were calculated and plotted against grafting time and shown in Figure 3. From the figure, it can be seen that grafting percentages (%) increased sharply with more grafting time until 9 h for cellulose and 12 h for MCC and then increased very slowly. From Figure 3, we consider 9–12 h as the best reaction time. Grafting percentages of MCC are higher than that of cellulose.

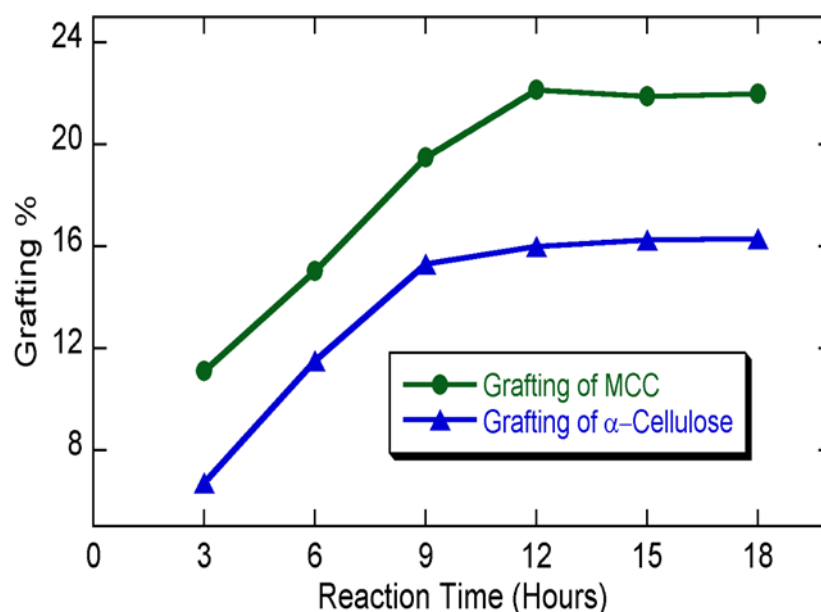


Figure 3. Grafting percentages of OLLA onto α -cellulose and MCC at different reaction time.

3.3. FTIR Spectroscopy Analysis

FTIR spectroscopic analysis is the most frequent technique to study intermolecular and intramolecular interaction in polymers and composites [44] and in this work, it is carried out to investigate intermolecular and intramolecular hydrogen bonding of α -cellulose, grafted α -cellulose, MCC and grafted MCC (Table 2).

Table 2. Prominent peaks of α -cellulose, grafted α -cellulose, MCC, and grafted MCC based on their FTIR spectra and possible bond for the absorption.

Bond for the Absorption (cm ⁻¹)	α -Cellulose (cm ⁻¹)	Grafted α -Cellulose (cm ⁻¹)	MCC (cm ⁻¹)	Grafted MCC (cm ⁻¹)
(3600–2500) –OH stretching	3385	3381	3402	3439
(3100–2900) –CH stretching (Asym)	2891	2895	2893	2902
(1780–1650) –C=O stretching	-	1728	-	1732
(1200–1020) –C–O– stretching	1026	1037	1049	1057

Figure 4 depicts the FTIR spectra of α -cellulose, grafted α -cellulose, MCC, and grafted MCC. Judging by the spectra analysis of OLLA grafted cellulose and MCC, the strongest carbonyl peak was observed at 1728 cm⁻¹ and 1732 cm⁻¹, respectively, which is absent in cellulose and MCC. This may confirm the grafting of OLLA onto cellulose and MCC surfaces which supported by the reported FTIR results for grafting of cyclic monomer (caprolactone and lactide) onto cellulose surfaces [19,45]. There is no change of broad –OH stretching peaks for α -cellulose and grafted α -cellulose and were observed at 3385 and 3381 cm⁻¹, respectively. However, in MCC (3402 cm⁻¹) and grafted MCC (3439 cm⁻¹) the wave number is shifted to the higher wave number. This may be attributed to the hydrogen bonded to hydroxyl groups on the grafter MCC [19]. Past studies have supported this results [46,47]. The presence of C–H stretching peaks at 2891 cm⁻¹ and 2893 cm⁻¹ of α -cellulose and MCC correspond to the amorphous part of samples [19]. The C–H stretching peaks of cellulose shifted to a higher wave number 2891 cm⁻¹ to 2895 cm⁻¹ after grafting OLLA. Similarly, the other bending peak was shifted to the higher wave number due to the formation of an intermolecular bond [36]. C–O– stretching peaks of cellulose were shifted from 1026 cm⁻¹ to 1037 cm⁻¹, whereas for MCC the peaks were shifted from 1049 cm⁻¹ to 1057 cm⁻¹ after grafting. Most of the characteristic absorption peaks of the grafted cellulose and MCC shifted to a higher wave number when the peak area is increased [48]. In addition, the reduction of peak intensity of α -cellulose and MCC were around 1100–1400 cm⁻¹, which may be due to the partial removal of hemicellulose and lignin. Wang et al. supported this finding [49].

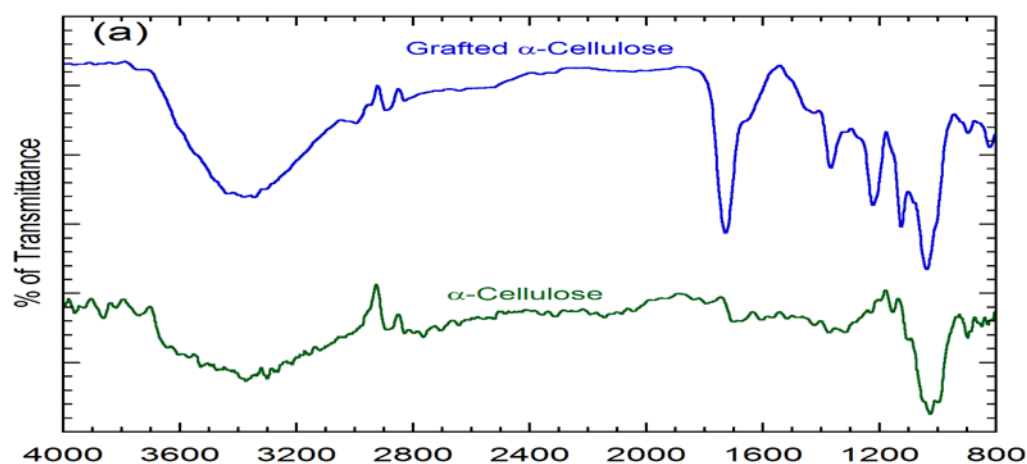


Figure 4. Cont.

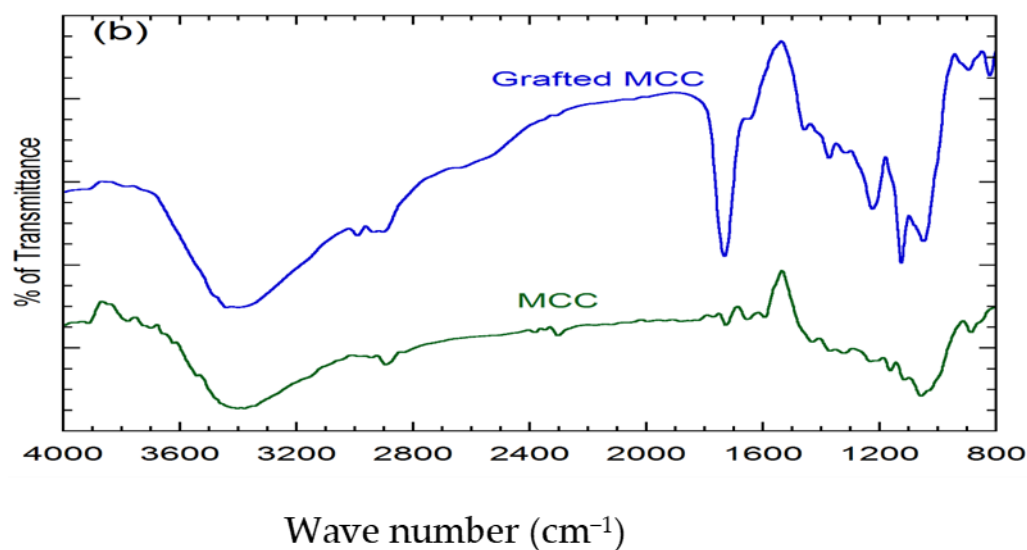


Figure 4. FTIR Spectra of α -cellulose and grafted α -cellulose (a), and MCC and grafted MCC (b).

3.4. SEM Analysis

SEM photographs of non-grafted and grafted α -cellulose and MCC are shown in Figure 5. Grafting of OLLA on to α -cellulose and MCC can be observed in Figure 5a–d, respectively. Grafted surfaces of α -cellulose and MCC are different from non-grafted surfaces, which confirms the grafting of OLLA and is consistent with the FTIR results [50]. Surfaces of the grafted MCC are more interesting (i.e., surface grafted area is higher when they are compared to the grafted α -cellulose).

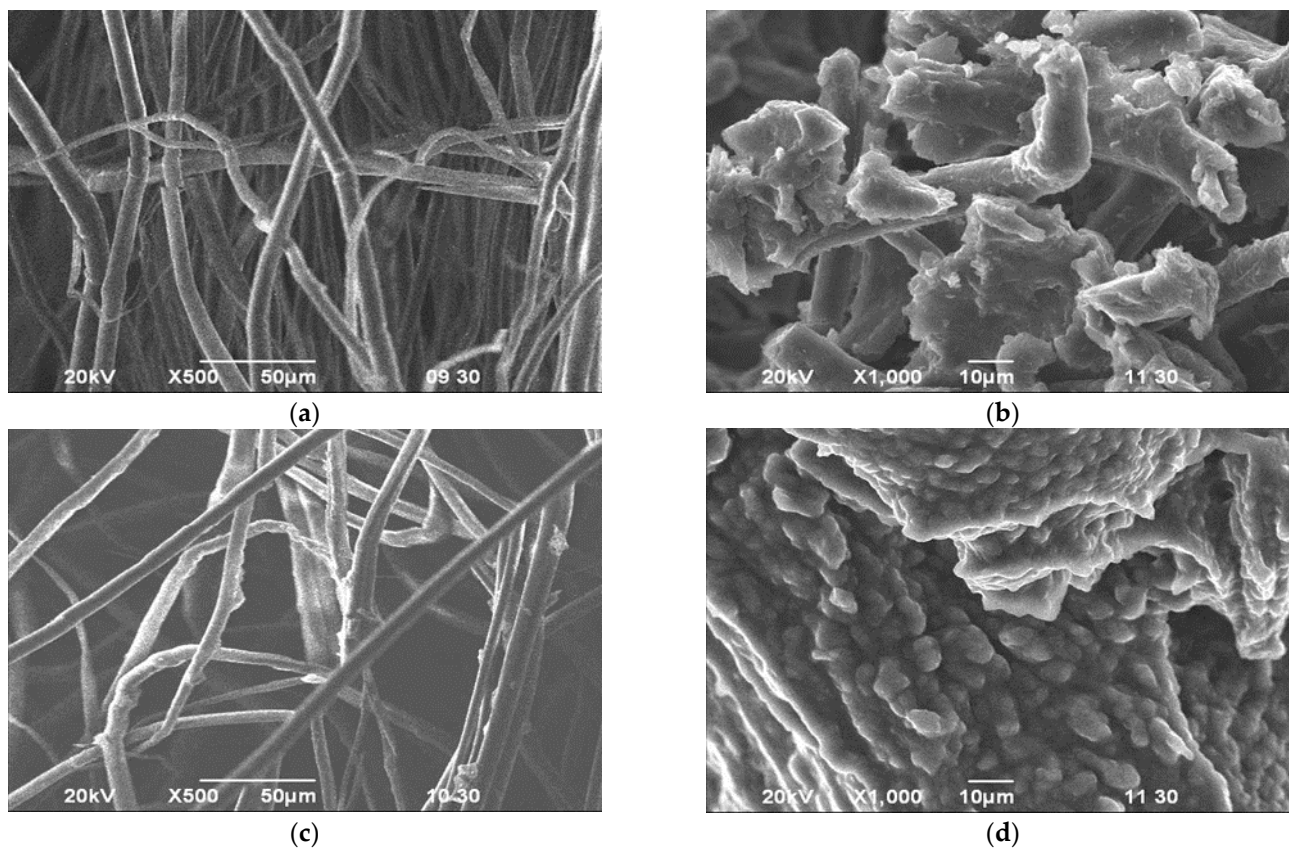


Figure 5. Non-grafted (a,b) and grafted (c,d) α -cellulose and MCC, respectively.

3.5. WAXS Analysis

Crystallinity in α -cellulose is a prominent characteristic contributing to its physical, chemical, and mechanical properties. WAXS profiles of non-grafted and grafted α -cellulose and MCC are shown in Figure 6. From Figure 6a, the diffraction pattern of α -cellulose shows a characteristic broad peak area between 2θ values 20 – 40° which supports cellulose's reported diffraction [51,52]. These characteristic peaks of cellulose indicate that crystallinity is very low and the characteristic peak of MCC shows a higher intensity at 22.5° with a diminishing amorphous peak area, supporting previously reported results [51].

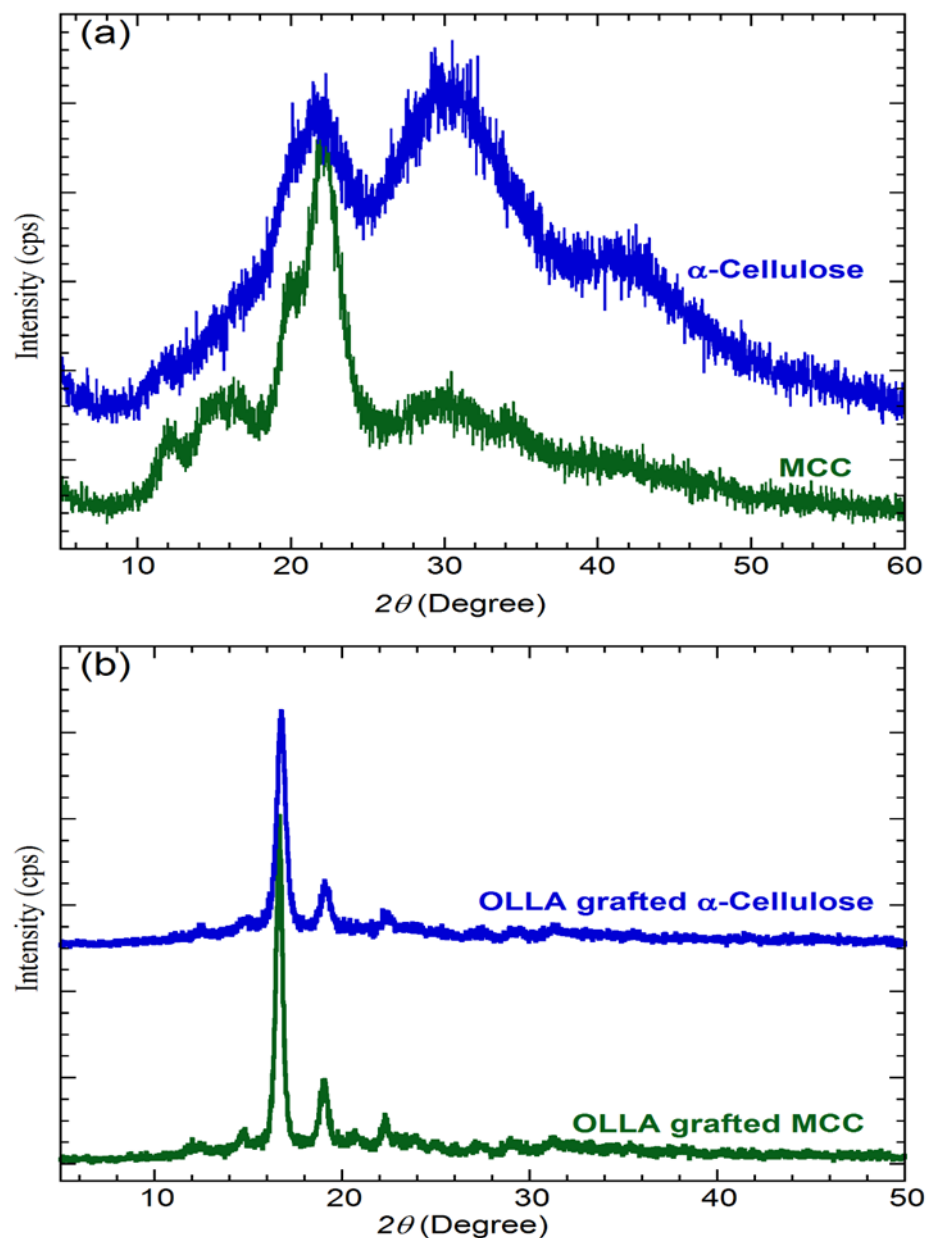


Figure 6. WAXS spectra of α -cellulose and MCC: non-grafted (a), and grafted (b).

The crystallinity in α -cellulose, MCC, grafted α -cellulose, and grafted MCC were calculated to 27.1%, 39.5%, 46.7% and 60.6%, respectively. The crystallinity of PLLA was reported to 47.6% by Dai et al. (2020) [53]. It is suggested here that the crystallinity of MCC is higher than that of α -cellulose. Grafted α -cellulose and MCC show sharp peaks at 16.7° and 19.0° and small peaks at 22.4° . Peaks at 16.7° and 19.0° were caused by the homo crystalline structure of pseudo-orthorhombic unit cell with dimensions of $a = 1.07$ nm,

b = 0.595 nm and c = 2.78 nm containing 10^3 helical structures. These two characteristic peaks are similar to what has been reported for PLLA homo crystallinity [54]. This also supports the grafting of OLLA on the surface of cellulose and MCC.

4. Conclusions

OLLA was synthesized with a controlled molecular weight of M_n $1.8\text{--}2.6 \times 10^2 \text{ g.mol}^{-1}$. Grafting of α -cellulose and MCC with OLLA were successfully carried out and confirmed by FTIR and SEM studies. The optimum grafting reaction time amounted to 9–12 h and grafting percentages were higher for MCC than that of cellulose. New characteristic absorption peaks appeared at 1728 cm^{-1} and 1732 cm^{-1} in the spectrum of grafted α -cellulose and MCC, respectively. This can be explained based on the hypothesis that OLLA is grafted with MCC by forming a bond with –OH groups of MCC forming new functional groups (C=O). This information can provide a confirmation of grafting of cellulose and MCC with OLLA. SEM images of non-grafted cellulose and MCC and grafted cellulose and MCC highlight the different surface morphologies, and may confirm grafting of OLLA onto cellulose and MCC. Crystallinity of MCC is higher than that of α -cellulose and grafted α -cellulose whereas MCC showed sharp peaks at 16.7° and 19.0° with a small peak appearing at 22.4° . Thus, the grafted MCC could be more practical in applicability, such as in drug delivery systems, biomedical applications, and ecological foods packaging, when compared to cellulose.

Author Contributions: M.H.R.: conceptualization, data curation, formal analysis, funding acquisition, methodology, project administration, resources, supervision, validation, visualization, writing—original draft, writing—review and editing; M.A.H.: data curation, funding acquisition, investigation, formal analysis, visualization, writing—original draft; M.A.R.: methodology, investigation, formal analysis, visualization, resources, writing—extensively review and editing, submission; M.M.R.: data curation, funding acquisition, investigation, formal analysis; M.M.P.: writing—review and editing; S.M.N.A.: writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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