

Biocomposites of Poly(Lactic Acid) and Microcrystalline Cellulose: Influence of the Coupling Agent on Thermomechanical and Absorption Characteristics

Emre Gorgun, Alamry Ali, and Md. Saiful Islam*



Cite This: *ACS Omega* 2024, 9, 11523–11533



Read Online

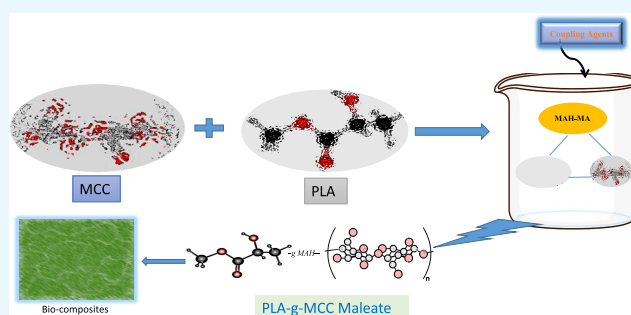
ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: In this study, poly(lactic acid) (PLA) and microcrystalline cellulose (MCC)-based green biocomposites were developed using a solution casting technique. Essentially, the bonding between PLA and MCC is quite feeble; therefore, the current study is conducted to strengthen the bonding by incorporating a coupling agent, thereby enhancing the overall quality of the biocomposites. Thus, the present study aimed to examine the influence of combined coupling agents—maleic anhydride (MAH) and maleic acid (MA) (MAH–MA)—on the properties of poly(lactic acid) (PLA)/microcrystalline cellulose (MCC) biocomposites. The investigation also encompassed an examination of the impact of MCC loading (2, 3, and 5% w/w)

into a PLA matrix. The Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) examination revealed the interfacial interaction and adhesion among MCC, PLA, and coupling agents and the formation of biocomposites. The incorporation of MAH–MA led to improved mechanical properties of the PLA/MCC biocomposites. Furthermore, the incorporation of MAH–MA into the PLA/3 wt % MCC composite exhibited enhancements in both the tensile strength and tensile modulus, accompanied by a reduced elongation at break. In addition, it is worth noting that the thermogravimetric analysis (TGA) curve of the PLA composite with 3% w/w of MCC and MAH–MA displayed a significant decrease in weight beyond a temperature threshold of 492.65 °C. The water absorption demonstrates that the incorporation of MAH–MA into the PLA/MCC composite led to advantageous water barrier characteristics. The observed improvements were attributed to the efficient dispersion of MCC at the most favorable amount of coupling agents, along with the chemical interactions involving grafting and esterification between MCC and the MAH–MA coupling agent. Furthermore, the incorporation of MAH–MA into the PLA/3% (w/w) MCC composite exhibited enhancements in both the tensile strength and tensile modulus, accompanied by a reduction in the elongation percentage at break. The experimental results about water absorption demonstrate that the incorporation of MAH–MA into the PLA/MCC composite led to advantageous water barrier characteristics. These improvements were attributed to good MCC dispersion and the chemical interactions involving grafting and esterification between the MCC and the MAH–MA coupling agent.



1. INTRODUCTION

The field of science and technology is currently shifting toward using renewable raw materials that are both ecologically friendly and sustainable. Biopolymers, such as cellulose, chitin, chitosan, and starch, are considered not only sustainable resources but also possess appealing characteristics and functionalities.^{1–3} Biopolymers are macromolecules composed of repeating subunits called monomers, arranged in linear, branched, or complex structures, and have a high molecular weight. Furthermore, it should be noted that biopolymers possess the desirable characteristics of being both biodegradable and renewable substances, presenting distinct advantages compared to their synthetic polymer counterparts.⁴ Blending biopolymers or their derivatives with other polymers can generate novel

composite materials that exhibit improved characteristics and find diverse applications across several fields.

Cellulose is a prominent biopolymer widely distributed and plentiful in many plant-based materials such as wood, cotton, and hemp. It serves as a predominant reinforcing agent in different matrices.⁵ In addition, there has been an increasing scholarly focus on the advancement of cellulose-based materials in recent decades, owing to their intriguing features. Zakaria et

Received: October 29, 2023

Revised: February 3, 2024

Accepted: February 9, 2024

Published: February 29, 2024



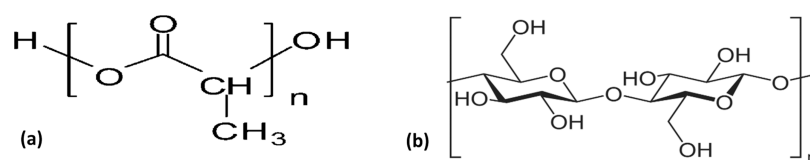


Figure 1. Molecular structure of (a) poly(lactic acid) and (b) microcrystalline cellulose (MCC).

al. and his co-authors conducted research work on the development of polylactic acid (PLA) as a sustainable substitute for traditional polymers derived from petroleum sources.⁶ In addition, it is noteworthy that polylactic acid (PLA) is recognized as a highly biodegradable thermoplastic material. PLA is a polyester derived from L-lactic acid (LA), which is created by the fermentation process of corn starch and other polysaccharide sources.⁷ Poly(lactic acid) (PLA) is a weakly hydrophobic polymer (contact angle of around 75°) that is derived from renewable feedstocks of agricultural origin. These feedstocks undergo fermentation to produce lactic acid, which is subsequently polymerized to form PLA. Furthermore, polylactic acid (PLA) exhibits considerable promise in packaging due to its ability to produce rigid films with excellent clarity and compatibility with commonly used manufacturing techniques.⁸ However, the thermal characteristics, toughness, water vapor, and gas barrier qualities of biodegradable polymers are shown to be less favorable compared to traditional petroleum-based polymers.⁹ To mitigate this issue, the incorporation of a coupling agent serves to augment the gas barrier by leveraging the combined effects of synergistic tortuosity, crystal nucleation, and chain immobilization.¹⁰ In addition, incorporating renewable and biodegradable fillers, such as cellulose or cellulose derivatives, can enhance the cost-performance equilibrium and augment the mechanical and thermal properties.^{11,12}

Microcrystalline cellulose (MCC) is a processed wood pulp variant with a natural fibrous structure characterized by its exceptionally high specific surface area.¹³ Microcrystalline cellulose (MCC) finds applications as drug-shaping and tablet-disintegrating agents within the medical and pharmaceutical sectors.¹⁴ Moreover, MCC exhibits thixotropic and thickening properties, making it suitable for use as a thickening agent and emulsifying agent in water-based coatings. Additionally, MCC possesses the ability to combine filling, thickening, and emulsifying functions, and demonstrates effective emulsification of oily substances. Due to its attributes of extensive biodegradability, robust stiffness, and elevated crystallinity, MCC has the potential to serve as a reinforcing agent for enhancing the mechanical properties and thermal stability of polymers.^{15,16} The user has provided a numerical reference without any accompanying text or context. The effectiveness of MCC in enhancing the capabilities of the PLA was also observed. Furthermore, it is worth noting that fragments of microcrystalline cellulose have a propensity to form cohesive bonds in the absence of any adhesive. Additionally, MCC can combine with various substances, enabling the retention of additives while simultaneously promoting self-adhesion. Pharmaceutical-grade tablets, including vitamins, pain medications, and other medicinal substances, can be manufactured.¹⁷ However, in recent times, the growing awareness of environmental issues has led material scientists to investigate the use of MCC as an eco-friendly filler in developing more environmentally sustainable polymer composites. The molecular structure of poly(lactic acid) and microcrystalline cellulose is shown in Figure 1.

Blending different materials to create composites has a significant benefit in terms of manipulating material properties and perhaps improving the material's inherent characteristics.¹⁸ Cellulose possesses desirable attributes of renewability, biodegradability, and a reasonably reactive surface. In addition, it has demonstrated that microcrystalline cellulose can be utilized to enhance the mechanical and thermal stability characteristics of PLA, while preserving the transparency of the matrix.¹⁹ The present trend in the packaging materials field involves advancing biobased and biodegradable alternatives. This is driven by the aim to minimize using nonrenewable and nonbiodegradable plastics, which pose significant environmental risks.²⁰ This assertion is also corroborated by those who advocate for the advancement of uncomplicated packaging formulas, with a special emphasis on blending tactics.⁷ Consequently, the incorporation of another biopolymer into PLA through the process of melt blending can result in substantial enhancements in the ultimate properties of the material. This approach offers a cost-effective, straightforward, and easily accessible method for processing. Furthermore, it is widely recognized that the compatibility of plasticizers and polymers is a significant challenge in achieving efficient plasticization. The process of blending modification involved the alteration of both the structure and microscopic composition of the microcrystalline cellulose system by the utilization of nonchemical linkages. This resulted in enhancing macroscopic mechanical properties, specifically the tensile strength and elongation at break. The improvement in mechanical properties resulting from the incorporation of MCC can be attributed to several factors, including its increased surface area, heightened activity, and the formation of hydrogen bonds between PLA and MCC. These factors collectively contribute to the uniform dispersion of MCC throughout the PLA matrix and provide a strong link between MCC and the boundary surface of PLA.^{19,20} Phosphoramides and polyphosphonate containing Schiff base (PVP) reagents enhanced the mechanical strength, toughness, and flame-retardant properties of PLA through the cross-linking reaction as reported recently by Xue et al. in 2021 and Xue et al. in 2023.^{21,22}

Microcrystalline cellulose can undergo various chemical alterations, such as esterification and grafting, to alter its thermal stability, mechanical properties, crystallinity, and other related characteristics. The incorporation of modified microcrystalline cellulose into polylactic acid (PLA) has been explored for a wide range of applications, including but not limited to food packaging, liquid containers, plastic bags, and disposable cups.^{23,24} The surface characteristics of cellulose fibers were modified by grafting polymerization, specifically through the "grafting from" free radical polymerization technique. This modification was typically achieved using carbamate or interlayer adsorption. Zhu and colleagues successfully synthesized methacrylic acid grafted microcrystalline cellulose (MA-MCC) using a grafting polymerization technique to produce an MA-MCC/PLA composite.²⁵ The study revealed that MA-MCC exhibited superior compatibility and dispersion within the

PLA matrix, resulting in enhanced tensile strength of the PLA composite. Consequently, the modified MCC enhanced its mechanical characteristics and decreased crystallization temperature. Incorporating coupling agents is imperative in PLA/cellulose composites as they play a crucial role in enhancing the composite material's compatibility, mechanical characteristics, thermal stability, and environmental resistance. Using these materials can lead to the development of a composite material that exhibits improved performance characteristics and a wider range of potential applications. Achieving optimal compatibility between the polymer matrices, specifically polylactic acid (PLA) and cellulose fillers, might provide significant challenges.

The compatibility between PLA and MCC is poor due to their different chemical natures, resulting in weak interfacial adhesion and reduced performance of the biocomposites. In this context, coupling agents can improve the interfacial adhesion between PLA and MCC by modifying their surface properties and enhancing interaction.^{26,27} Thus, incorporating coupling agents could significantly improve the mechanical, thermal, and barrier properties of PLA/MCC biocomposites.²⁶ As of today, there are many coupling agents such as silane, maleic anhydride (MAH), maleic acid (MA), isocyanate, triazine, etc., and various combinations of cellulose and polymers have been widely used in biocomposites and received excellent outcome.²⁸ Among these coupling agents, MAH and MA exhibit promising potential as suitable candidates for enhancing the overall characteristics of composites.^{26–29} Maleic anhydride plays a vital role in PLA-based biocomposites as a coupling agent, bridging the gap between the hydrophilic nature of natural fibers and the hydrophobic nature of polymer matrices. It reacts with hydroxyl groups on the surface of natural fibers (i.e., cellulose, lignin) through esterification or etherification reactions. The grafting reaction of maleic anhydride on fibers can increase surface roughness. Maleic acid is often employed as a coupling agent or compatibilizer in polymer blends and composite systems to enhance the adhesion between dissimilar materials. The maleic acid functionality can react with functional groups on the polymer matrix and reinforcing fillers, promoting better interfacial bonding. On the other hand, silane coupling agents possess a unique bifunctional structure. Its organofunctional group can react with various functional groups on natural fibers (i.e., hydroxyl, amine) through covalent bonding like silanol condensation and grafting.

Combining MAH and MA can act synergistically as a coupling agent in composite materials. Both MAH and MA contain reactive functional groups (carboxylic acid and anhydride groups) that can undergo chemical reactions with hydroxyl or amino groups present on the surface of reinforcing fillers or polymers. This coupling agent functionality helps improve the interfacial adhesion between the polymer matrix and the filler, enhancing the composite material's mechanical and thermal properties.

Several studies have been undertaken to examine the physical, mechanical, and thermal characteristics of composites comprising polylactic acid (PLA) and microcrystalline cellulose (MCC).^{11,17,20} Nevertheless, there has been a scarcity of research undertaken on the advancement of PLA/MCC/MAH–MA biocomposites and the exploration of their physicomechanical and thermal characteristics.^{2,12,30} Therefore, the primary aim of this study is to investigate the influence of the coupling agent (MAH–MA) and varying amounts of MCC loading on the properties of PLA/MCC biocomposites. The current study focused on the fabrication of biocomposites

comprising polylactic acid (PLA) and microcrystalline cellulose (MCC) with different weight percentages (2, 3, and 5% w/w) by a solution mixing and solvent casting method. Furthermore, a coupling agent was incorporated at the optimum weight percentage of microcrystalline cellulose (MCC).

2. MATERIALS AND METHODS

2.1. Materials. The chemicals utilized in this study were analytical reagents (AR grade, 99.9% purity). The pelletized variant of polylactic acid (PLA) was obtained from NatureWork LLC, situated in Minnetonka, MN. The material demonstrates a particular 1.24 g/cm³ density and a melt flow index (MFI) of g/10 min (190 °C/2.16 kg). The reinforcing filler used in this study was microcrystalline cellulose (MCC) sourced from Sigma Aldrich, a well-known commercial supplier. The MCC powder UFC100 was supplied by J. Rettenmaier Sohne. The MCC powder had an average particle diameter within a range of 6–12 μm and a bulk density of 0.15–0.2 g cm⁻³. The powdered microcrystalline cellulose (MCC) fibers, a reinforcing filler (particle size = 20 μm, pH = 5–7, bulk density = 0.5 g/mL at 25 °C) was purchased from Sigma Aldrich. The coupling agent utilized in this study was maleic anhydride (MAH) and maleic acid (MA), both obtained from Sigma Aldrich. The chloroform solvent employed in this experimental procedure was procured from R&M Chemicals.

2.2. Preparation of Pure PLA Film, PLA/MCC, and PLA/MCC/MAH–MA Biocomposites. PLA solution is prepared at 10% w/w concentration in chloroform by agitating the solution in a water bath maintained at a temperature of 60 °C until complete dissolution of the PLA pellets occurs. After that, the PLA solution was evenly applied onto a Petri dish at ambient temperature for a duration of 24 h to allow for the evaporation of the solvent. The measured thickness of the cast solution was approximately 100 μm. Subsequently, the film that was produced was carefully detached from the surface on which it was cast.

To prepare PLA/MCC biocomposites, 10% (w/w) PLA pellets and 2% (w/w) MCC were added to chloroform solution in two different beakers. After that, 2% (w/w) MCC solution is added to the PLA solution. The solution was agitated in a water bath maintained at a temperature of 60 °C until complete dissolution of the PLA and MCC blend was achieved. After that, the PLA/MCC solution was equally distributed onto a Petri dish at ambient temperature for 24 h to allow for the evaporation of the solvent. The procedure is replicated for MCC concentrations of 3 and 5% (w/w). The measured thickness of the cast solution was approximately 100 μm. Subsequently, the formed film was carefully detached from the surface on which it had been cast.

To prepare PLA/MCC/MAH–MA biocomposites, 10% (w/w) PLA pellets and 2% (w/w) MCC were added to chloroform solution in two different beakers. At the same time, 0.1% (w/w) MAH and 0.05% (w/w) MA were dissolved in chloroform, maintaining a ratio of 2:1 between MAH and MA. Subsequently, the entirety of the solution was combined and subjected to stirring in a water bath maintained at a temperature of 60 °C until complete dissolution of PLA, MCC, and MAH–MA was achieved. The suspension was then sonicated for 2 min in order to avoid sedimentation, and then the solution was equally distributed onto a Petri dish at ambient temperature and allowed to evaporate for 24 h. The thickness of the cast solution was found to be around 100 μm. Consequently, the formed film was carefully detached from the surface on which it was cast. The

created composites were subsequently tested to evaluate their morphological characteristics, mechanical strength, and thermal stability. The formulations of various biocomposites and their synthesis process are presented in Table 1 and Figure 2 respectively.

Table 1. Formulations of Different Composites

types of composites	% (w/w) of PLA	% (w/w) of MCC	% (w/w) of MAH	% (w/w) of MA
PLA	10.00			
PLA/2 wt % MCC	10.00	2		
PLA/3 wt % MCC	10.00	3		
PLA/5 wt % MCC	10.00	5		
PLA/3 wt % MCC/MAH-MA	10.00	3	0.10	0.05

2.3. Fourier Transform Infrared Spectroscopy (FTIR). The materials were subjected to FTIR examination using a PerkinElmer 1725X spectrometer. The samples were crushed and ground into powder and combined with KBr before being compacted into pellets.

2.4. Scanning Electron Microscopy (SEM). The surface morphology of the sample was determined using a JEOL Model JSM-6400 scanning electron microscope (SEM) made in Japan. The samples were placed on the stub and coated with gold. The images were scanned at a magnification of 500X.

2.5. Mechanical Test. A mechanical test assessed the modulus, strength, and elongation at break of the pure PLA film and blend composite films. The test was carried out using a Shimadzu Universal Testing Machine with a loading capacity of 5 kN, following the guidelines specified in ASTM D882.

2.6. Thermogravimetric Analysis (TGA). The thermal stability of the samples was assessed using a PerkinElmer thermogravimetric analyzer. The analysis was conducted under a nitrogen environment, with a heating rate of 10 °C/min, spanning a temperature range from 50 to 700 °C. A quantity of approximately 2 mg was utilized to analyze each sample, and subsequently, the weight reduction of the samples was ascertained.

2.7. Water Absorption. Following the guidelines set by ASTM D570, spherical specimens with a diameter of 6 mm were manufactured for each distinct composite. The specimens underwent a drying process in an oven set at a temperature of 60 °C for 1 h, after which they were allowed to cool in a desiccator. The specimens were promptly weighed once they had cooled

down and then placed in deionized water at room temperature for 24 h. The specimens were extracted, gently dried, and measured in terms of weight. Following the process of weighing, the specimens were subsequently submerged back into the water and subjected to reweighing over 10 consecutive days. The measurement of water absorption is quantified by the percentage increase in weight and is determined using the formula presented in eq 1

$$\text{water absorption (\%)} = \frac{w_2 - w_1}{w_1} \times 100\% \quad (1)$$

where w_1 is the dry weight of the specimen, and w_2 is the wet weight of the specimen. Five test specimens were prepared for this test, and the results were averaged.

3. RESULTS AND DISCUSSION

3.1. Fourier Transform Infrared Spectroscopy (FTIR).

An FTIR test was conducted to investigate the interaction between PLA, MCC, and a couple of agents. Researcher Haafiz and his co-workers stated that the FTIR test is perfect for investigating the intermolecular interaction and phase behavior between the polymer and cellulose fibers.³¹ In this study, the interaction between PLA/MCC and coupling agents was investigated by FTIR spectroscopy and is shown in Figure 3.

The distinctive peaks of pure polylactic acid (PLA) are depicted in Figure 3, revealing strong bending peaks within the 3330–3600 cm^{-1} range. The observed signal at 1757 cm^{-1} can be attributed to the C=O stretching vibration of the carbonyl group. The observed peaks within the wavenumber range from 2946 to 2999 cm^{-1} can be attributed to the asymmetric stretching vibration of the C–H bonds. Additionally, the observed peaks at 1448 cm^{-1} might be related to the deformation of the carbon–hydrogen (C–H) bonds in the CH_3 group. Furthermore, peaks due to the presence of carbon–carbon (C–C) single bonds were seen at 920 and 871 cm^{-1} . Based on the analysis of spectrum 4 (b), it is evident that introducing MCC into PLA did not result in significant alterations in the FTIR peaks. The narrow peak intensity observed at 1757 cm^{-1} corresponds to the presence of the carbonyl group (C=O) upon adding MCC. The observed phenomenon was ascribed to the physical interaction between PLA and MCC, rather than a chemical interaction, as reported.³² The peak observed at 1757 cm^{-1} , which corresponds to the C=O functional group, exhibits significant broadening as the proportion of MCC (microcrystalline cellulose) added is

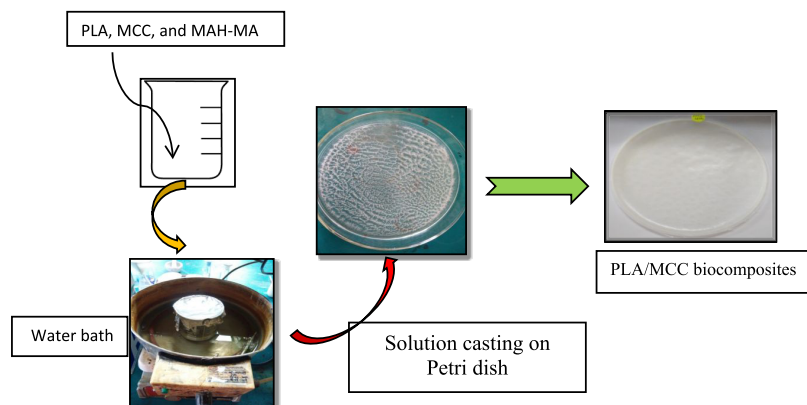


Figure 2. Synthesis process of PLA/MCC biocomposites.

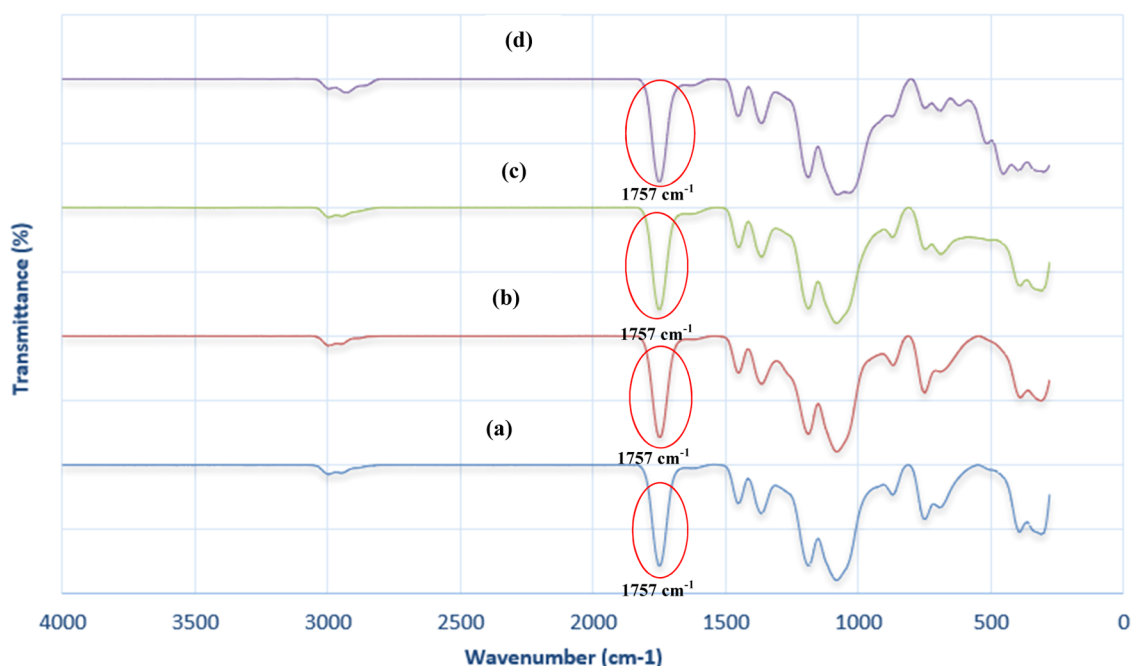
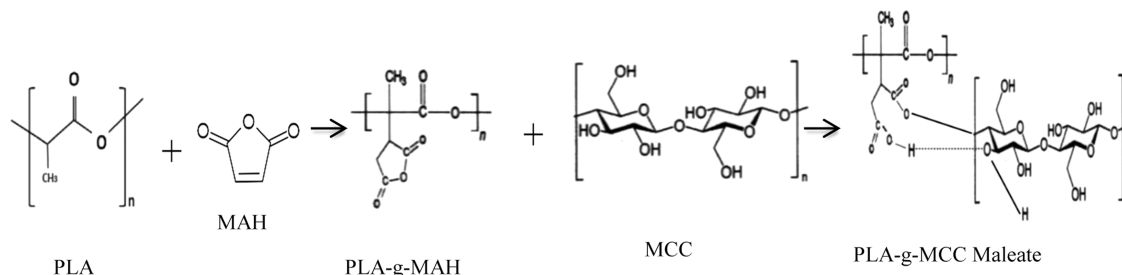
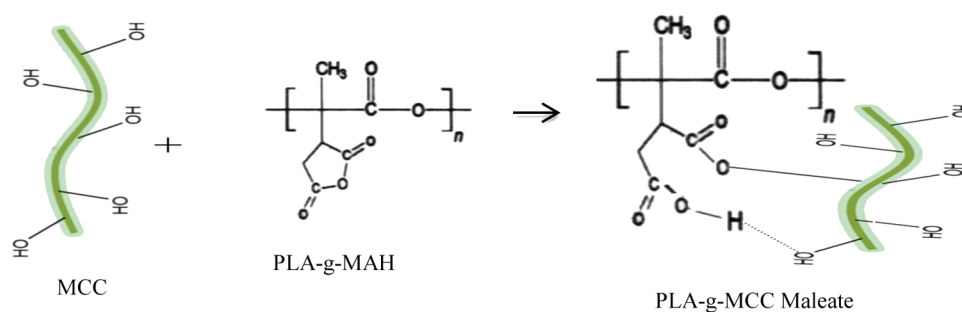


Figure 3. FTIR spectra of (a) pure PLA, (b) PLA/2 wt % MCC, (c) PLA/3 wt % MCC, and (d) PLA/3 wt % MCC/MAH-MA biocomposites.

Scheme 1. Reaction Mechanism between PLA and MCC in the Presence of the Coupling Agent (MAH)



Scheme 2. Maleate-Functionalized PLA Reacts with the Hydroxyl Groups on the Surface of MCC, Forming Ester Linkages between PLA and MCC^a



^aIn general: PLA/MCC + MAH-MA → PLA-g-MCC maleate.

increased. The observed phenomenon can be due to the interaction between the carbonyl group (C=O) of polylactic acid (PLA) and the hydroxyl groups (O-H) of microcrystalline cellulose (MCC). Notably, the presence of coupling agents MAH-MA in the PLA/MCC polymer matrix leads to the broadening of the relatively tiny peaks at 3100 cm^{-1} , which are attributed to the alcoholic group (-OH). Furthermore, the presence of coupling agents leads to robust and broad peaks at around 1050 cm^{-1} , which can be attributed to the CO-O-CO stretching vibration of the anhydride compound. This suggests

that a chemical interaction occurs between cellulose and coupling agents. Other researchers have also reported comparable findings when employing a coupling agent to bond cellulose fiber and polymer.³³ The reaction between maleic anhydride and maleic acid occurs with the hydroxyl (-OH) groups on the cellulose chains, forming ester linkages and ultimately yielding the cellulose maleate product. Based on the assertion mentioned above, the subsequent possible chemical reaction involving MCC and coupling agents was postulated in Schemes 1 and 2.³³

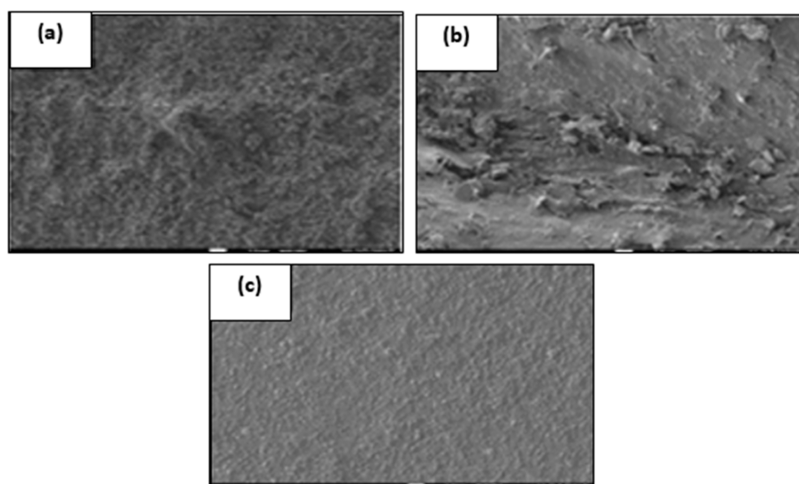


Figure 4. SEM images of (a) PLA, (b) PLA/3 wt % MCC, and (c) PLA/3 wt % MCC/MAH–MA biocomposites. (Magnification at 500 \times).

3.2. Scanning Electron Microscopy (SEM). The SEM analysis was conducted to gain insights into the microstructure and interfacial morphology of PLA- and MCC-based biocomposites. Figure 4 shows the SEM images of PLA, PLA/MCC, and PLA/MCC/MAH–MA biocomposites. SEM images revealed the microstructure of the biocomposites at 500 \times magnifications. As can be seen in Figure 4a the morphology of the PLA fractured surface is covered with uneven fibrils and a number of microvoids throughout the surface. Thus, ductile fracture could be considered for the fractured surface of pure PLA.²²

The SEM image of the PLA/3 wt % MCC biocomposite revealed some gaps and weak interfaces between the PLA and MCC phases. This is due to the poor interaction and bonding between PLA and MCC. On the other hand, SEM micrographs of PLA/3 wt % MCC/MAH–MA biocomposites show a smooth surface texture. This result is expected because the coupling agents promoted better adhesion at the interface, as evidenced by reduced voids and improved filler–matrix interactions, as seen in Figure 4c. The presence of MAH–MA coupling agents led to a more homogeneous and integrated microstructure, contributing to enhanced mechanical and thermal properties. Moreover, the introduction of coupling agents visibly impacted interfacial adhesion, leading to improved dispersion and reduced agglomeration of MCC within the PLA matrix.¹⁹ Coupling agents played a crucial role in enhancing the compatibility between PLA and MCC. The SEM micrographs showed a more uniform distribution of MCC particles in the presence of coupling agents, indicating improved interfacial bonding. Surface modifications attributed to the coupling agents were evident, influencing the overall morphology and interphase characteristics. The SEM results collectively indicate that coupling agents positively influence the microstructure and interfacial properties of PLA and MCC biocomposites.

3.3. Mechanical Results. Tensile properties of pure PLA, PLA/MCC, and PLA/MCC/MAH–MA biocomposites were investigated in order to find the effect of different compositions of MCC which is 2, 3, and 5% w/w. Moreover, the effect of the addition coupling agent, MAH–MA, to the PLA/3% w/w MCC composite is determined. Figure 5 shows a typical stress–strain curve for the pure PLA composite. Figures 6, 7, and 8 illustrate the tensile strength, tensile modulus, and percentages of elongation at break of pure PLA, PLA/MCC composites with varying amounts of MCC loading, and PLA/MCC/MAH–MA.

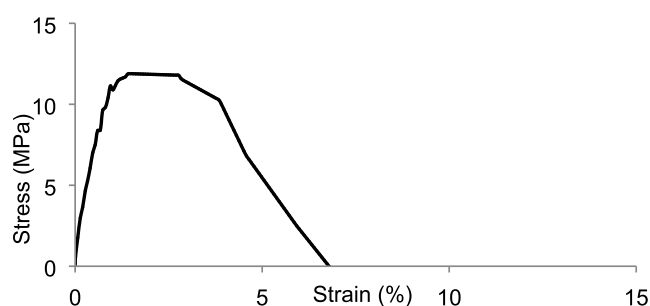


Figure 5. Typical stress–strain curve of pure PLA.

Previous studies conducted by Das et al. in 2011 indicated that achieving a uniform dispersion of highly suitable filler materials can enhance interaction with the polymer matrix.³⁴ This, in turn, can contribute to improvements in the composites' mechanical integrity and thermal stability. However, from this study, the tensile strength of composites decreased upon the addition of MCC as a reinforcement filler, as shown in Figure 6. A decrease in tensile strength could be attributed to a weak interfacial interaction between PLA and MCC.^{1,35} This statement is also supported by the reduction of tensile strength after the addition of MCC due to agglomeration, which leads to poor interaction at the interphase.³⁶ Furthermore, the decrease in tensile strength of PLA/MCC composites might be attributed to the inadequate stress transmission across the interphase, resulting in a lack of interfacial bonding between the cellulose reinforcement and the polymer matrix.³⁷ The inadequate bonding between the matrix and fiber results in the formation of many voids at the interface, compromising the efficient transmission of stress to the load-bearing fibers. Consequently, this leads to diminished strength properties. After the coupling agent is added to the PLA/3% MCC composite, the tensile strength is increased compared to the composite of PLA/3% MCC. This shows that interfacial adhesion between PLA and MCC was significantly improved.³⁸

Incorporating microcrystalline cellulose (MCC) served as a reinforcing filler and exhibited favorable interactions with various polymers, leading to enhancements in the tensile modulus. The PLA/MCC composites exhibit reduced tensile strength and elongation at break compared to pure PLA. Furthermore, it is worth noting that the PLA/MCC composites exhibit a slightly elevated level of stiffness compared to pure PLA. The bar graph illustrates a clear relationship between the

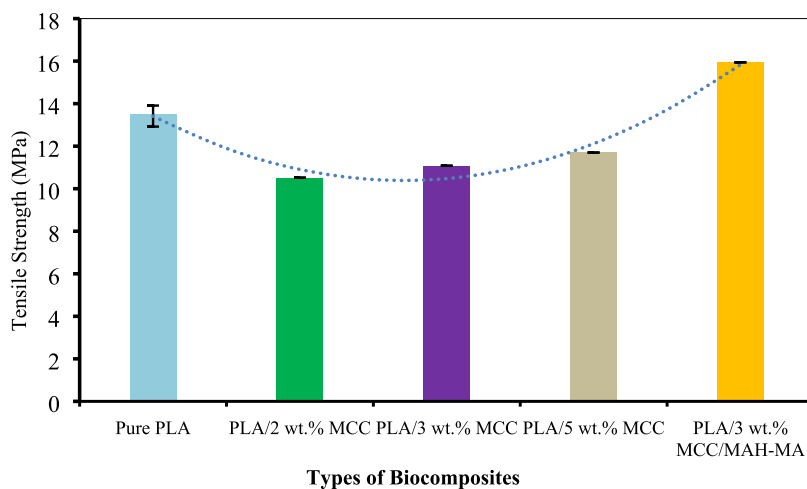


Figure 6. Tensile strength of different biocomposites.

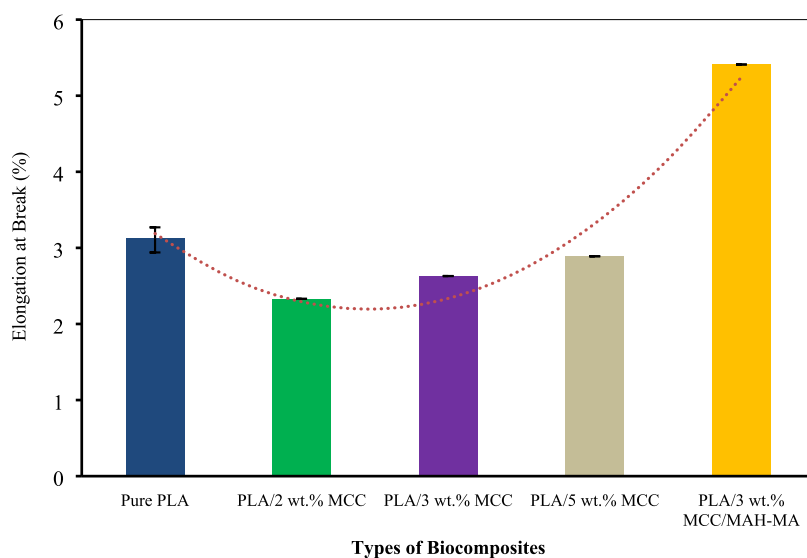


Figure 7. Elongation at break of different biocomposites.

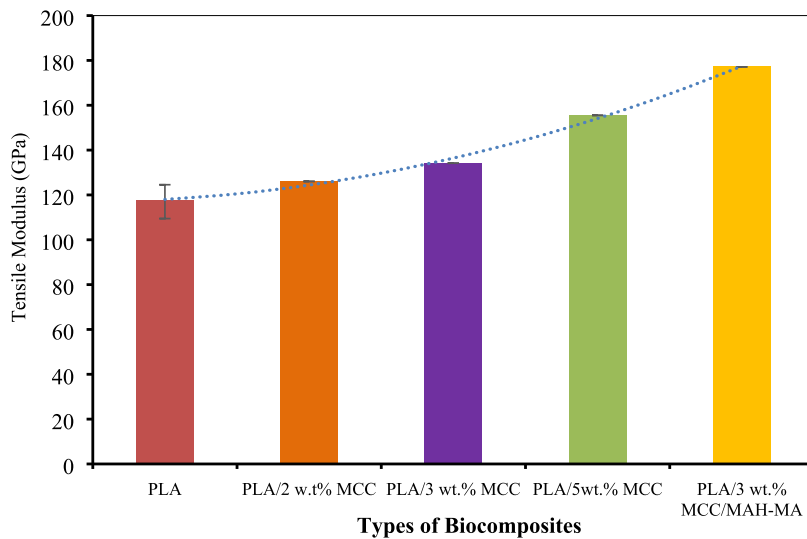


Figure 8. Tensile modulus of different biocomposites.

composition of MCC and its impact on the strength of composites compared to pure PLA. A rise in MCC composition

leads to a decrease in composite strength. However, it is worth noting that there is a tiny increase in modulus with higher MCC

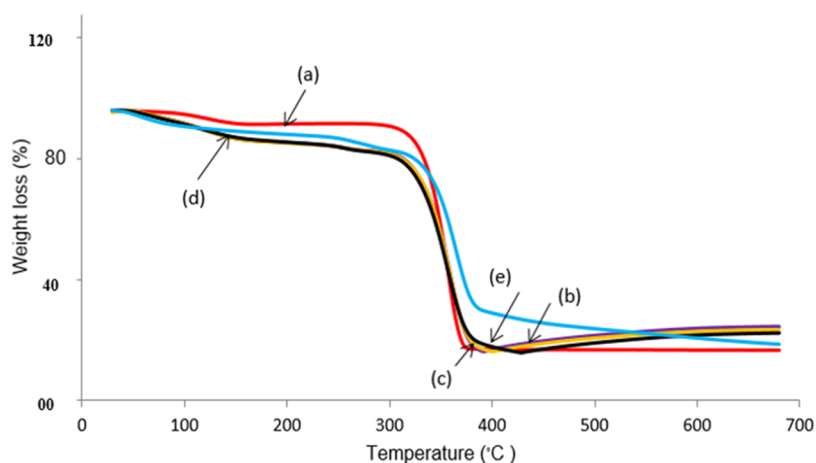


Figure 9. TGA thermograms of (a) PLA, (b) PLA/2 wt % MCC, (c) PLA/3 wt % MCC, (d) PLA/5 wt % MCC, and (e) PLA/3 wt % MCC/MAH–MA biocomposites.

Table 2. Maximum Temperature, Onset Temperature, and Percentage of Decomposition of Different Biocomposites

types of composites	onset temperature (°C)	maximum degradation temperature, T_{max} (°C)	percentage of decomposition (%)
PLA	296	382	93.4
PLA/2 wt % MCC	293	398	89.7
PLA/3 wt % MCC	297	406	87.9
PLA/5 wt % MCC	298	426	87.0
PLA/3 wt % MCC/MAH–MA	310	493	74.0

composition. This is due to the MCC fibers' intrinsic stiffness contributing to the overall modulus. Moreover, the reinforcing effect of the fibers constrains matrix deformation. The interfacial interactions and void formation are increased when MCC is added, and thus, the strength of the composite decreases. When there is a decrease in tensile strength, this might be accompanied by a refinement or modification of the material's microstructure. This alteration can contribute to an increase in Young's modulus, reflecting changes in the material's ability to deform under stress.

According to the findings of this research study, all the composites consisting of PLA/MCC exhibited a greater tensile modulus in comparison to pure PLA. Specifically, the composite containing 5 wt % MCC demonstrated the highest modulus, followed by the composite with 3 wt % MCC, and finally, the composite containing 2 wt % MCC. However, in this particular instance, it can be argued that the modulus of 2 wt % MCC and 3 wt % MCC are statistically equivalent, given the incorporation of standard deviations into the analysis. The findings from the mechanical testing indicate that all composites of PLA/MCC exhibit a greater modulus compared to pure PLA. Nevertheless, including the coupling agent MAH–MA resulted in a greater modulus than PLA/MCC alone. The brittleness of PLA, a polymer, appears to be enhanced by incorporating microcrystalline cellulose. The tensile strength of pure polylactic acid (PLA) is greater in comparison to PLA composites containing microcrystalline cellulose (MCC) and PLA composites containing combined MAH and MA coupling agent.^{39,40}

It is anticipated that some additional elements that impact the mechanical properties of the investigated composites will influence how well composites operate mechanically. First, the PLA matrix has the ability to adhere to the cellulosic reinforcements and the interphase is effective at transferring stress. Additionally, the aspect ratio and volume proportion of the reinforcements also impact the mechanical properties. The

level of crystallinity of the matrix comes last but certainly not least.⁴¹

The PLA, a semicrystalline polymer, is anticipated to exhibit enhanced crystallinity by incorporating cellulosic reinforcement. The presence of these crystalline zones has the potential to serve as physical cross-links or filler particles, hence leading to a significant enhancement in the modulus. The increased modulus seen in the PLA/MCC and PLA/MCC/MAH–MA composites in comparison to pure PLA may suggest a reduction in crystallinity inside the pure PLA composite. In the process of fabricating PLA/MCC composites, it is seen that the cooling rate is rapid, leading to a mostly amorphous matrix. The presence of crystallinity in the composites is attributed mainly to the trans-crystallinity of the PLA on the surface of the fibers.³⁷

3.4. Thermal Analysis. Figure 9 shows TGA thermograms of various biocomposites, and important values for degradation were calculated and tabulated in Table 2. TGA analysis provides data on degradation-induced weight loss as a function of temperature. TGA was utilized in this research to look into the thermal behavior of pure PLA, PLA/MCC, and PLA/MCC/MAH–MA biocomposites. According to research, the highest thermal deterioration rate occurs at a temperature known as the first decomposition temperature, also known as the onset temperature and the maximum degradation temperature (T_{max}).⁴²

It can be seen from Figure 9 that the degradation peak of pure PLA began at 296 °C and was entirely decomposed at 382 °C with a decomposition percentage of 93.4%. According to Table 2, the PLA/MCC composite has greater onset degradation temperatures than pure PLA. This suggests that when compared to pure PLA, PLA/MCC composites have improved thermal stability. The PLA/MCC composites' thermal degradation temperature commenced at 293 °C and increased to 297 and 298 °C for loadings of 3 and 5% (w/w) of MCC, respectively.

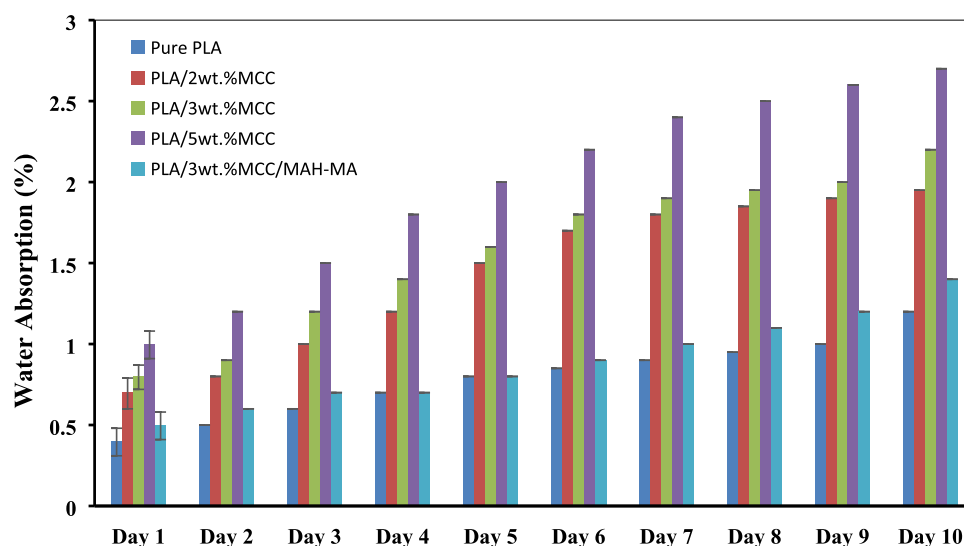


Figure 10. Percentage of water absorption of pure PLA, PLA/2 wt % MCC, PLA/3 wt % MCC, PLA/5 wt % MCC, and PLA/3 wt % MCC/MAH-MA biocomposites.

Furthermore, the thermal stability of the PLA/MCC blend was improved when MAH-MA was added.

When the MCC content is increased from 2 to 5% (w/w), both the T_{\max} and the onset temperature rise dramatically. T_{\max} for the PLA/3 wt % MCC blend was found to be 8 °C higher than that of the 2 wt % MCC blends. T_{\max} for a PLA/5 wt % MCC composite is 426 °C, up from 405 °C for a composite containing 3 wt % MCC. In addition, the breakdown rates of PLA/3 and 5 wt % MCC are very identical at 87.9 and 87.0%.

The onset temperature of the PLA/3 wt % MCC composite was raised to 310 °C with the addition of dispersed MAH-MA. By reassembling it into a more stable structure, the surface of the blend is protected from the diffusion of volatile degradation products (small, gaseous molecules), which slows down the blend's degradation over time.⁴³

3.5. Water Absorption. Figure 10 depicts the water absorption properties of the produced composites. Because moisture absorption during immersion in water or exposure to high humidity is intimately related to composite properties such as mechanical strength, dimensional stability, and appearance, moisture absorption results are vital for understanding the performance of cellulose-based composites.

According to earlier studies, PLA is quickly hydrolyzed by moisture, and the obtained hydrolysis products are harmless to humans.⁴⁴ Water absorption can significantly impact the behavior of organic materials by causing chemical and physical changes. The assertion is substantiated by research that indicates that PLA can absorb up to 1% of its weight in water.⁴⁵

PLA, on the other hand, demonstrated adequate water resistance.⁴⁶ This statement has been supported by previous studies in which the PLA is suitable for usage as a hydrophobic component.⁴⁷ Figure 10 shows that the pure PLA film has negligible water absorption content ranging from 0.4–1.2% over a 10-day test period, demonstrating that PLA is medium water resistant.

Adding MCC to the film makes it possible to improve the mechanical properties of composites while reducing their ability to react. A test of the composite's overall water absorption was conducted. The rate of water absorption decreased with an increase in the number of MCC particles, but a further increase in the percentage of MCC particles reveals that the elevated

percentage of moisture absorption may be caused by poor mixing.⁴⁸

However, the water absorption of the PLA/MCC composite increased after blending with MCC and ranged from 0.7 to 2.7%. Despite the fact that MCC powder absorbs less water than the neat polymer, its inclusion in composites causes the moisture content to rise in contrast to the unfilled sample.^{49,50} Additionally, the MCC content of the composites is proportional to the rise in the moisture content.

Over the duration of the ten-day test period, the MAH-MA addition to the PLA/3 wt % MCC composite showed varying water absorption percentages. According to Figure 9, the PLA/3 wt % MCC/MAH-MA composite demonstrated lower water absorption than the PLA/3 wt % MCC mix composite, ranging from 0.5 to 1.4%. This suggested that adding MAH-MA to PLA/3 wt % MCC composite will result in materials with good water barrier qualities.

4. CONCLUSIONS

The solution casting method was successfully used to prepare PLA/MCC biocomposites. At various MCC loadings, it has been noted that the physical, mechanical, and thermal properties of PLA/MCC composites change. The mechanical and thermal properties of the PLA/MCC biocomposites have significantly improved as a result of the addition of a coupling agent, specifically maleic anhydride and maleic acid (MAH-MA), grafted onto to the PLA and MCC (i.e., PLA-g-MCC). FTIR analysis was used to verify the coupling agent's inclusion into the PLA/MCC composite. This finding also implies that PLA/MCC and MAH-MA have strong attraction and interaction. This finding also suggests that the hydroxyl (–OH) groups on the cellulose chains are involved in the reaction between MAH and MA, which results in the formation of ester bonds and the production of the cellulose maleate as biocomposites. The SEM results revealed that coupling agents significantly modified the surface structure and enhanced interfacial interaction between PLA and MCC of composites. The PLA/3 wt % MCC composite's mechanical strength increased as a result of the addition of the coupling agent. The efficient, attractive interaction between the composite parts is responsible for the improvement. According to the TGA result, the incorporation of

a coupling agent increased the temperature at which the matrix decomposition occurred and improved thermal stability. The developed composite showed improved water barrier properties after MAH–MA was added to the PLA/3 wt % MCC biocomposite.

AUTHOR INFORMATION

Corresponding Author

Md. Saiful Islam – Department of Chemistry, Bangladesh Army University of Engineering and Technology, Natore 6431, Bangladesh; orcid.org/0000-0003-1579-9452; Email: mdsaifulislam16@bauet.ac.bd, msaifuli2007@gmail.com

Authors

Emre Gorgun – Department of Railway Systems, Sivas Cumhuriyet University, Sivas 58040, Turkey
Alamry Ali – Department of Mechanical Engineering, College of Engineering in Al-Kharj Prince Sattam bin Abdulaziz University, Al-Kharj 11942, Saudi Arabia

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.3c08448>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Department of Chemistry, Bangladesh Army University of Engineering and Technology for research support.

REFERENCES

- (1) Zhang, Y.; Zhang, Y.; Xu, W.; Wu, H.; Shao, Y.; Han, X.; Zhou, M.; Gu, P.; Li, Z. Preparation methods of cellulose nanocrystal and its application in treatment of environmental pollution: A mini-review. *Colloids Interface Sci. Commun.* **2023**, *53*, No. 100707.
- (2) Ren, H.; Xu, Z.; Gao, M.; Xing, X.; Ling, Z.; Pan, L.; Tian, Y.; Zheng, Y.; Fan, W.; Yan, W. Preparation of microcrystalline cellulose from agricultural residues and their application as poly(lactic acid)/microcrystalline cellulose composite films for the preservation of Lanzhou lily. *Int. J. of Biol. Macromol.* **2023**, *227*, 827–838.
- (3) Sharifi, A.; Mousavi, S. R.; Ghanemi, R.; Mohtaramzadeh, Z.; Asheghi, R.; Mohammadi-Roshandeh, J.; Khonakdar, H. A.; Hemmati, F. Extruded biocomposite films based on poly(lactic acid)/chemically-modified agricultural waste: Tailoring interface to enhance performance. *Int. J. Biol. Macromol.* **2023**, *233*, No. 123517.
- (4) Sadegh-Hassani, F.; Nafchi, A. M. Preparation and characterization of bionanocomposite films based on potato starch/halloysite nanoclay. *Int. J. Biol. Macromol.* **2014**, *67*, 458–462.
- (5) Zhang, Q.; Lei, H.; Cai, H.; Han, X.; Lin, X.; et al. Improvement on the properties of cellulose/poly(lactic acid) composites by using activated biochar. *J. Cleaner Prod.* **2020**, *252*, No. 119898.
- (6) Zakaria, Z.; Islam, M. S.; Hassan, A.; Haafiz, M. K. M.; et al. Mechanical properties and morphological characterization of PLA/chitosan/epoxidized natural rubber composites. *Adv. Mater. Sci. Eng.* **2013**, *2013*, No. 629092.
- (7) Zhao, Bo.; Zhang, Yi.; Ren, H. Effects of microcrystalline cellulose surface modification on the mechanical and thermal properties of poly(lactic acid) composite films. *Plast., Rubber Compos.* **2020**, *49* (10), 450–455.
- (8) Qian, S.; Kong, Y.; Cheng, H.; Tu, S.; Zhai, C. Interfacial interaction improvement of poly(lactic acid)/bamboo-char biocomposites for high toughness, good strength, and excellent thermal stability. *Surf. Interfaces* **2023**, *42*, No. 103315.
- (9) Tang, Y.; Yang, H.; Vignolini, S. Recent progress in production methods for cellulose nanocrystals: leading to more sustainable processes. *Adv. Sustainable Syst.* **2022**, *6* (3), No. 2100100.
- (10) Martino, V. P.; Ruseckaite, R. A. Correlation between composition, structure and properties poly(lactic acid)/polyadipate-based nano-biocomposites. *Macromol. Mater. Eng.* **2010**, 551–558.
- (11) Ren, H.; Li, S.; Gao, M.; et al. Preparation and Characterization of Microcrystalline Cellulose/Poly(lactic acid) Biocomposite Films and Its Application in Lanzhou Lily (*Lilium davidii* var. unicolor) Bulbs Preservation. *Sustainability* **2023**, *15* (18), No. 13770.
- (12) Paul, U. C.; Fragouli, D.; Bayer, I. S.; et al. Effect of green plasticizer on the performance of microcrystalline cellulose/poly(lactic acid) biocomposites. *ACS Appl. Polym. Mater.* **2021**, *3* (6), 3071–3081.
- (13) Adel, A. M.; El-Wahab, Z. H. A.; Ibrahim, A. A.; Al-Shemy, M. T. Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part II: Physicochemical properties. *Carbohydr. Polym.* **2011**, *83*, 676–687.
- (14) Kong, Y.; Qian, S.; Zhang, Z.; Tian, J. The impact of esterified nanofibrillated cellulose content on the properties of thermoplastic starch/PBAT biocomposite films through ball-milling. *Int. J. Biol. Macromol.* **2023**, *253*, No. 127462.
- (15) Yang, C.; Zhu, Y.; Tian, Z.; Zhang, C.; Han, X.; Jiang, S.; Liu, K.; Duan, G. Preparation of nanocellulose and its applications in wound dressing: A review. *Int. J. Biol. Macromol.* **2024**, *254*, No. 127997.
- (16) Lin, N.; Huang, J.; Chang, P. R.; Feng, J.; Yu, J. Surface acetylation of cellulose nanocrystal and its reinforcing function in poly(lactic acid). *Carbohydr. Polym.* **2011**, *83*, 1834–1842.
- (17) Hanna, M.; Biby, G.; Miladinov, V.; U.S. Patent and Trademark Office. Production of Microcrystalline Cellulose by Reactive Extrusion. U.S. Patent US6,228,213, 2001.
- (18) Ali, N. A.; Noori, F. T. M. Crystallinity, mechanical, and antimicrobial properties of poly(lactic acid)/microcrystalline cellulose/silver nanocomposites. *Int. J. Appl. Innovation. Eng. Manage.* **2014**, 77–81.
- (19) Bhasney, S. M.; Kumar, A.; Katiyar, V. Microcrystalline cellulose, poly(lactic acid) and polypropylene biocomposites and its morphological, mechanical, thermal and rheological properties. *Composites, Part B* **2020**, *184*, No. 107717.
- (20) Li, X.; Lin, Y.; Liu, M.; Meng, L.; Li, C. A review of research and application of poly(lactic acid) composites. *J. Appl. Polym. Sci.* **2023**, *140* (7), No. e53477.
- (21) Xue, Y.; Zhang, T.; Tian, L.; Feng, J.; Song, F.; Pan, Z.; Song, P.; et al. A molecularly engineered bionanocomposite polyphosphonate containing Schiff base towards fire-retardant PLA with enhanced crystallinity and mechanical properties. *Chem. Eng. J.* **2023**, *472*, No. 144986.
- (22) Gong, M.; Zhao, Q.; Dai, L.; Li, Y.; Jiang, T. Fabrication of poly(lactic acid)/hydroxyapatite/graphene oxide composite and their thermal stability, hydrophobic and mechanical properties. *J. Asian Ceram. Soc.* **2017**, *5*, 160–168.
- (23) Dong, F.; Yan, M. L.; Jin, C. D.; Li, S. J. Characterization of type-II acetylated cellulose nanocrystals with various degree of substitution and its compatibility in PLA films. *Polymer* **2017**, *9*, No. 346, DOI: 10.3390/polym9080346.
- (24) Li, H.; Cao, Z.; Wu, D.; Tao, G.; Zhong, W.; Zhu, H.; Qiu, P.; Liu, C. Crystallisation, mechanical properties and rheological behaviour of PLA composites reinforced by surface modified microcrystalline cellulose. *Plast., Rubber Compos.* **2016**, *45*, 181–187.
- (25) Zhu, T.; Guo, J.; Fei, B.; Feng, Z. Y.; Gu, X. Y.; et al. Preparation of methacrylic acid modified microcrystalline cellulose and their applications in poly(lactic acid): Flame retardancy, mechanical properties, thermal stability and crystallization behavior. *Cellulose* **2020**, *27*, 2309–2323.
- (26) González-López, M. E.; Robledo-Ortiz, J. R.; Manríquez-González, R.; Silva-Guzmán, J. A.; Pérez-Fonseca, A. A. Poly(lactic acid) functionalization with maleic anhydride and its use as coupling agent in natural fiber biocomposites: a review. *Compos. Interfaces* **2018**, *25* (5–7), 515–538.
- (27) Chen, K.; Li, P.; Li, X.; Liao, C.; Li, X.; Zuo, Y. Effect of silane coupling agent on compatibility interface and properties of wheat

- straw/poly(lactic acid) composites. *Int. J. Biol. Macromol.* **2021**, *182*, 2108–2116.
- (28) Anbupalani, M. S.; Venkatachalam, C. D.; Rathanasamy, R. Influence of coupling agent on altering the reinforcing efficiency of natural fibre-incorporated polymers—A review. *J. Reinf. Plast. Compos.* **2020**, *39* (13–14), 520–544.
- (29) Ma, P.; Jiang, L.; Ye, T.; Dong, W.; Chen, M. Melt free-radical grafting of maleic anhydride onto biodegradable poly(lactic acid) by using styrene as a comonomer. *Polymers* **2014**, *6* (5), 1528–1543.
- (30) Singh, A. A.; Genovese, M. E.; Mancini, G.; Marini, L.; Athanassiou, A. "Green processing route for poly(lactic acid)-cellulose fiber biocomposites. *ACS Sustainable Chem. Eng.* **2020**, *8* (10), 4128–4136.
- (31) Haafiz, M. M.; Hassan, A.; Zakaria, Z.; Inuwa, I. M.; Islam, M. S.; Jawaid, M. Properties of poly(lactic acid) composites reinforced with oil palm biomass microcrystalline cellulose. *Carbohydr. Polym.* **2013**, *98*, 139–145.
- (32) Qu, P.; Gao, Y.; Wu, G.; Zhang, L. Nanocomposites of poly(lactic acid) reinforced with cellulose nanofibrils. *BioResources* **2010**, *5*, 1811–1823.
- (33) Oliver-Ortega, H.; Reixach, R.; Espinach, F. X.; Méndez, J. A. "Maleic anhydride poly(lactic acid) coupling agent prepared from solvent reaction: synthesis, characterization and composite performance. *Materials*. **2022**, *15* (3), No. 1161.
- (34) Das, K.; Ray, D.; Bandyopadhyay, N. R.; Sahoo, S.; Mohanty, A. K.; Misra, M. Physico-mechanical properties of the jute micro/nanofibril reinforced starch/poly(vinyl alcohol) biocomposite films. *Composites, Part B* **2011**, *42* (3), 376–381.
- (35) Rayung, M. I.; Ibrahim, N.; Zainuddin, N.; et al. The effect of fiber bleaching treatment on the properties of poly(lactic acid)/oil palm empty fruit bunch fiber composites. *Int. J. Mol. Sci.* **2014**, *15* (8), 14728–14742.
- (36) Díez-Pascual, A. M.; Naffakh, M.; Gómez, M. A.; Marco, C.; Ellis, G.; Gonzalez-Dominguez, J. M.; Ansón, A.; et al. The influence of a compatibilizer on the thermal and dynamic mechanical properties of PEEK/carbon nanotube composites. *Nanotechnology* **2009**, *20* (31), No. 315707.
- (37) Mathew, A. P.; Oksman, K.; Sain, M. Mechanical properties of biodegradable composites from poly(lactic acid) (PLA) and microcrystalline cellulose (MCC). *J. Appl. Polym. Sci.* **2005**, *97* (5), 2014–2025.
- (38) Zhang, J. F.; Sun, X. Mechanical properties of poly(lactic acid)/starch composites compatibilized by maleic anhydride. *Biomacromolecules* **2004**, *5* (4), 1446–1451.
- (39) Gao, C.; Wu, Y.; Xie, H. "Fully Bio-Based Composites of Poly(Lactic Acid) Reinforced with Cellulose-Graft-Poly(ϵ -Caprolactone) Copolymers. *J. Renewable Mater.* **2023**, *11* (3), 1137–1152.
- (40) Ye, G.; Li, Z.; Chen, B.; et al. "Performance of poly(lactic acid)/polycaprolactone/microcrystalline cellulose biocomposites with different filler contents and maleic anhydride compatibilization. *Polym. Compos.* **2022**, *43* (8), 5179–5188.
- (41) Dufresne, A.; Dupeyre, D.; Paillet, M. Lignocellulosic flour-reinforced poly(hydroxybutyrate-co-valerate) composites. *J. Appl. Polym. Sci.* **2003**, *87* (8), 1302–1315.
- (42) Li, Z.; Jiang, W. T. A thermogravimetric investigation of alkylammonium intercalation into rectorite. *Thermochim. Acta* **2009**, *483* (1), 58–65.
- (43) Silverajah, V. S. G.; Ibrahim, N. A.; Zainuddin, N.; Yunus, W. M. Z. W.; Hassan, H. A. Mechanical, thermal and morphological properties of poly(lactic acid)/epoxidized palm olein blend. *Molecules* **2012**, *17* (10), 11729–11747.
- (44) Garlotta, D. A Literature Review of Poly(Lactic Acid). *J. Polym. Environ.* **2002**, *9*, 63–84.
- (45) Finkenstadt, V. L.; Liu, C. K.; Evangelista, R.; Liu, L.; Cermak, S. C.; Hojilla-Evangelista, M.; Willett, J. L. Poly(lactic acid) green composites using oilseed coproducts as fillers. *Ind. Crops Prod.* **2007**, *26* (1), 36–43.
- (46) Martin, O.; Schwach, E.; Couturier, Y. Properties of Biodegradable Multilayer Films Based on Plasticized Wheat Starch. *Starch-Stärke* **2001**, *53*, 372–380.
- (47) Suyatma, N. E.; Copinet, A.; Tighzert, L.; Coma, V. Mechanical and barrier properties of biodegradable films made from chitosan and poly(lactic acid) blends. *J. Polym. Environ.* **2004**, *12* (1), 1–6.
- (48) El Deeb, R.; El Messiry, M. Mechanical and water absorption properties of micro-cellulose obtained from cotton fiber waste reinforced poly(vinyl alcohol) (PVA) composites. 2015, pp 234–244.
- (49) Cataldi, A.; Dorigato, A.; Deflorian, F.; Pegoretti, A. Effect of the water sorption on the mechanical response of microcrystalline cellulose-based composites for art protection and restoration. *J. Appl. Polym. Sci.* **2014**; Vol. 131 18.
- (50) Rahman, M. M.; Islam, M. S.; Li, G. S. Development of PLA/CS/ZnO nanocomposites and optimization its mechanical, thermal and water absorption properties. *Polym. Test.* **2018**, *68*, 302–308.