

Biodegradable polylactic acid/polyhydroxybutyrate-co-hydroxyvalerate blend composites with microcrystalline cellulose – mechanical, rheological and thermal investigation

Kamil Badura^{1,2*} , Patrycja Bazan³ 

¹ CUT Doctoral School, Faculty of Material Engineering and Physics, Cracow University of Technology, 31-155 Krakow, Poland

² SHM System Sp. z o.o., Sp. kom. Libertów, ul. Jana Pawła II 82A, 30-444 Kraków, Poland

³ Faculty of Material Engineering and Physics, Cracow University of Technology, 31-155 Krakow, Poland

* Corresponding author's e-mail: kb@shmsystem.pl

ABSTRACT

The primary objective of the study was to conduct mechanical, dynamic, thermal, and rheological analyses of composites based on PLA/PHBV blends. Specifically, three composites were produced with microcrystalline cellulose content at 5, 10, and 15 wt.%. These materials were also subjected to aging tests. The findings of the study reveal the strengthening effect of microcrystalline cellulose and its positive impact on resistance to environmental factors. However, it is important to note that an excessive amount of filler decrease strength properties and processing issues. Despite this limitation, the study demonstrates the significant potential for using microcellulose and biodegradable PLA/PHBV blends to create high-strength, environmentally friendly polymer composites.

Keywords: biodegradable composites, mechanical properties, rheological properties, PLA/PHBV blend, microcellulose.

INTRODUCTION

The production of plastics worldwide has witnessed a substantial increase over the past decade. In 2021, the global production of plastics was estimated to have exceeded 390 million metric tons [1] while in 2019 was 359 million metric tons of plastic, which shows the increasing trend of plastic production [2]. It is utilized in various industries such as packaging, construction, textiles, consumer products, and others [3, 4].

The continuous rise in plastic production leads to an alarming accumulation of waste in the environment. By 2050, global plastic waste production is estimated to surpass 12,000 million tonnes, reflecting the growing dependence on plastics [5, 6]. Over 40% of the produced plastic is utilized for single-use packaging, which significantly exacerbates the waste issue [7]. The accumulation of plastic waste poses a severe threat

to the environment, causing the pollution of ecosystems [8]. The inadequate waste management practices and low recovery rates aggravate the pollution problem, especially in the oceans [9]. The COVID-19 pandemic has further intensified the plastic waste crisis by increasing the volume of waste [10]. Despite efforts to tackle the problem, the production and leakage of plastic into the environment are projected to persist and increase [11]. Currently, between 22% and 43% of the world's plastic waste ends up in landfills, with adverse environmental consequences [12]. As the largest producer and consumer of plastics, China significantly contributes to the problem [13].

The continuous production of plastics and waste generation emphasize the need to develop a sustainable strategy for managing this raw material. The exploration of materials with a lower environmental impact, the integration of renewable energy sources in the production process, and

research into biorefineries that can facilitate the production of plastics from various raw materials should be considered [14].

Bioplastics and biocomposites are increasingly being seen as a viable alternative to traditional petroleum-based plastics due to their numerous advantages. Bioplastics, frequently derived from renewable resources, are more biodegradable and compostable than traditional plastics [15]. They are a key component of the circular economy contributing to more sustainable life cycles for these materials [16].

Bioplastics possess mechanical characteristics similar to those of conventional plastics, but they are derived from bio-based sources, making them biodegradable [15]. Their most significant advantage lies in their potential to decrease the mounting amount of plastic waste. By being biodegradable, bioplastics can degrade into environmentally friendly products through the action of specific microorganisms. This prevents the buildup of waste in the natural and industrial environments and promotes sustainability [17]. Bioplastics offer a more environmentally friendly alternative to non-biodegradable plastic waste by reducing it [18]. The production and use of bioplastics resulted in a lower carbon footprint and decreased reliance on fossil fuels, which supports climate change mitigation efforts [19]. Bioplastics versatility allows them to be used in a wide range of products, such as packaging materials, kitchen utensils, and automotive components [20].

Bioplastics offer several advantages, including their production from renewable resources such as starch or polylactic acid, which enhances their sustainability [21]. The development of bioplastics from organic waste and biomass presents an opportunity for a more sustainable future for the plastics industry. The utilization of raw materials like algae, cellulose, or food waste in bio-conversion processes can lessen environmental impact and promote efficient resource management [22]. For instance, the production of biopolymer films and biodegradable packaging materials using seaweed polysaccharides showcases the potential of bioplastics as an environmentally friendly alternative to conventional plastics [23]. Polylactic acid (PLA) and polyhydroxybutyrate-co-hydroxyvalerate (PHBV) are biodegradable polymers with various advantages in diverse applications. PLA, which is derived from resources such as corn starch or sugar cane, exhibits biocompatibility, biodegradability, and mechanical

properties comparable to traditional plastics [24]. PHBV, a type of polyhydroxyalkanoate (PHA) produced by bacteria, possesses good biodegradability and biocompatibility, making it suitable for biomedical applications [25].

The advantages of PLA include its renewable origin, biodegradability, and versatility, which make it suitable for use in packaging, biomedical implants, and tissue engineering scaffolds. PLA-based biocomposites exhibit improved mechanical properties, which increases their use in various industries due to their ecological nature. PLA is also often mixed with PHBV to enhance mechanical strength and biodegradability [26].

PHBV, as a biodegradable polyester, offers benefits such as minimizing the risk of inflammatory reactions in tissues, as its biodegradation products are components of human blood [25]. PHBV is used in tissue engineering, wound dressings, and ligament repair scaffolds, confirming its biocompatibility and potential in regenerative medicine [27, 28] PHBV blends with other polymers, such as PLA, have been developed to adapt the properties of materials to specific applications, for example, in bone tissue engineering and cartilage regeneration [29, 30].

The utilization of polylactic acid and polyhydroxybutyrate-co-hydroxyvalerate in biocomposites leads to materials with enhanced properties, which can be utilized for a broad range of applications. These blends exhibit improvements in mechanical properties, including tensile strength and modulus of Young [31], enhanced thermal stability, and tailored thermal properties and morphology, which are relevant for specific applications [32]. Additionally, these blends exhibit good biodegradability and partial miscibility, which affects their rheology, morphology, and barrier properties. The addition of PHBV to PLA also enhances processing properties by reducing brittleness and increasing melting strength [33]. As a result, blends of PLA and PHBV are versatile materials that can be utilized in industries such as packaging, biomedical engineering, and materials science.

This research aims to explore the effects of incorporating microcrystalline cellulose into polylactic acid and poly(hydroxybutyrate-valerate) blends. The objective is to enhance the mechanical and rheological properties of these biopolymer composites, which are garnering attention for their potential applications in sustainable materials and biodegradable plastics. By

investigating the interplay between cellulose content and composite behavior, the study seeks to identify optimal formulations that improve stiffness, flexibility, and resistance to aging while maintaining processability. Understanding these interactions is crucial for developing materials that meet performance standards and contribute to environmental sustainability. Previous research has acknowledged the benefits of cellulose as a reinforcement agent. For instance, Valle et al. investigated biodegradable biocomposites utilizing a PLA/PHB mixture as a matrix and two types of microcrystalline cellulose (MCC and sMCC) at 3, 5, and 7 wt.% as a filler. The study evaluated the influence of the type and content of cellulose on the thermal, morphological, and molecular dynamics properties of the materials. The findings indicated that the addition of cellulose did not significantly affect the temperatures of thermal transformations (T_m , T_c , T_{cc}). However, at 7 wt% filler, a decrease in the crystallinity and thermal stability of the matrix (PLA/PHB) was observed, which was attributed to the formation of filler aggregates. These results suggest a significant effect of the addition of microcellulose on the aging resistance of the composites [34].

The article is characterized by a novel approach to research on biocomposites incorporating MCC and their potential application in sustainable materials. The study comprehensively evaluates the impact of varying MCC concentrations on the mechanical, rheological, and aging properties of these composites. Previous research, such as that conducted by Valle and colleagues [34], was primarily limited to thermal and morphological analysis. This new approach provides a more comprehensive assessment of changes in material properties. The paper is among the first to elucidate the simultaneous mechanical reinforcement and stabilization of materials in terms of resistance to environmental degradation. This is crucial in the context of developing more durable and reliable biodegradable materials. The study makes a significant contribution to the advancement of biocomposites, offering a comprehensive

approach to optimizing their mechanical properties, processing, and durability, a critical step towards more sustainable materials of the future.

MATERIALS AND METHODS

Materials

The selected matrix material was a PLA/PHBV polyester blend comprised of 90% PLA and 10% PHBV, supplied by ColorFabb (Belfeld, The Netherlands). Nanografi Nano Technology (Jena, Germany) provided the reinforcement material, MCC (AceCel 102, SIGACHI®, India), which served as the reinforcement material. Polymer composites containing 5, 10, and 15% by weight of MCC were produced. The content of the additive was selected based on literature data. Polymer matrices' most widely used reinforcement contents are 5, 10, 15, 20% by weight. The global trend was used to compare the effects of reinforcement. Table 1 presents a description and density of the manufactured materials. The PLA/PHBV and its composites were fabricated through injection molding, and the processing parameters are presented in Table 2.

Methods of testing

Strength tests are of paramount importance as they serve as indicators of future research directions. In this study, both static tension and static bending tests were conducted. The Charpy method, which involves impact testing on unnotched specimens, was carried out using a Zwick/Roell HIT5.5P hammer (Ulm, Germany) in accordance with PN-EN ISO 179-1:2010. The static tensile test (PN-EN ISO 527-1:2010) and static bending test (PN-EN ISO 178:2011) were performed on a Shimadzu AGS-X 10 kN testing machine (Kyoto, Japan) with a test speed of 10 mm/min. All strength tests were repeated after the accelerated thermal aging process. The accelerated thermal aging process was carried out using an QUV

Table 1. Description of the materials produced

Designation	Description	Density (g/cm ³)
PLA/PHBV	PLA/PHBV blend containing 90% PLA and 10% PHBV as the base material	1.242 ± 0.004
5MCC	PLA/PHBV blend with 5 wt.% of microcrystalline cellulose	1.231 ± 0.003
10MCC	PLA/PHBV blend with 10 wt.% of microcrystalline cellulose	1.278 ± 0.001
15MCC	PLA/PHBV blend with 15 wt.% of microcrystalline cellulose	1.281 ± 0.001

Table 2. Injection molding parameters to produce testing specimens

Feed zone	Temperature (°C)						Injection pressure (bar)	Compression pressure (bar)	Press time (s)
	Zone 1	Zone 2	Zone 3	Zone 4	Nozzle	Mold			
50	180	180	185	190	185	30	1000	650	10

Accelerated Weathering Tester aging chamber (Q-LAB Corporation, Westlake, OH, USA). Method and parameters are described in detail in [35].

The fabrication of composites necessitated the development of mechanical hysteresis loops to provide insight into their viscoelastic properties. The study employed an applied load of up to 50% of the maximum breaking force identified during the tensile test of the weakest material. This procedure aimed to assess the displacement that occurs during repetitive use and the energy dissipation. The tests were carried out using a Shimadzu AGS-X 10 kN testing machine (Kyoto, Japan) equipped with Autograph Trapezium X software for energy dispersion analysis. The loading and unloading speed were set at 10 mm/min.

Differential scanning calorimetry (DSC) was conducted. Portions of the material, weighing 5.0 ± 0.2 mg, were measured using a RADWAG 22W laboratory balance (Radom, Poland) with a resolution of 0.01 mg and placed in an aluminum crucible. The DSC test was carried out using an instrument Netzsch DSC 404 F3 Pegasus (Selb, Germany). The study program comprised the following stages, which were repeated twice: (1) heating from -20 °C to 200 °C at a rate of 10 °C/min under a nitrogen atmosphere, (2) annealing at 200 °C for 10 minutes in a nitrogen atmosphere, and (3) cooling from 200 °C to -20 °C at 10 °C/min under nitrogen.

The evaluation of rheological properties in the low shear rate range was conducted using oscillatory rheometry on an Anton Paar MCR 302e (Graz, Austria) rotational rheometer in a parallel plate system with a diameter of 25 mm and a measuring gap of 1 mm. The measuring temperature was set according to the maximum temperature applied during stirring, which was 180 °C. Measurements were made with a strain of $\gamma = 0.05\%$, which was selected based on preliminary measurements made in the variable amplitude mode of measurement in the range of strain value $\gamma = 0.01$ – 100% and constant angular frequency $\omega = 10$ rad/s. The preliminary tests confirmed that the applied strain value remained within the range of linear viscoelasticity for all material series. The analysis of rheological properties was carried out

in the oscillation mode in the range of angular frequency $\omega = 0.5$ – 500 rad/s. Rheological tests were also conducted using the Goettfert RHEOGRAPH 120 (Buchen, Germany) capillary rheometer at a measurement temperature of 180 °C. Measurements were made using a cylindrical nozzle with a channel diameter of 2 mm and a length of 40 mm, and an entry angle of 120° . The previously dried material (Chemland vacuum drying oven, min. 24 hours, 60 °C) was placed in the rheometer cylinder and plasticized for 180 s. The composite was then extruded, and the pressure of the plasticized polymer composition was determined before entering the measuring nozzle at a specific volumetric flow rate. The tests were conducted in the shear rate range from 50 s⁻¹ to 900 s⁻¹ of the uncorrected shear rate. Due to the use of a nozzle with a ratio of $L/D = 20$, the Bagley correction was omitted.

The study employed a JEOL JSN5510LV (Tokyo, Japan) scanning electron microscope manufactured by JEOL Ltd. in Tokyo, Japan, for microscopic examinations. To ensure accurate results, the sample's surface was coated with a conductive gold layer using the JOEL JEE-4X vacuum evaporator, also produced by JEOL Ltd. in Tokyo, Japan, prior to testing.

RESULTS AND DISCUSSION

Mechanical investigation

The manufactured composites were subjected to fundamental tests of mechanical properties, and the results are illustrated in Figures 1–3. The research findings indicate that the addition of microcrystalline cellulose to PLA/PHBV blends has a positive impact on the stiffness and deformability of the composite. However, the study results suggest that an increase in strain was only observed for the material containing 5% of the additive by weight. A further increase in the content of the additive resulted in a decrease in deformation at break. The incorporation of microcellulose also led to a decrease in bending strength and tensile strength. Nevertheless, as the fiber content

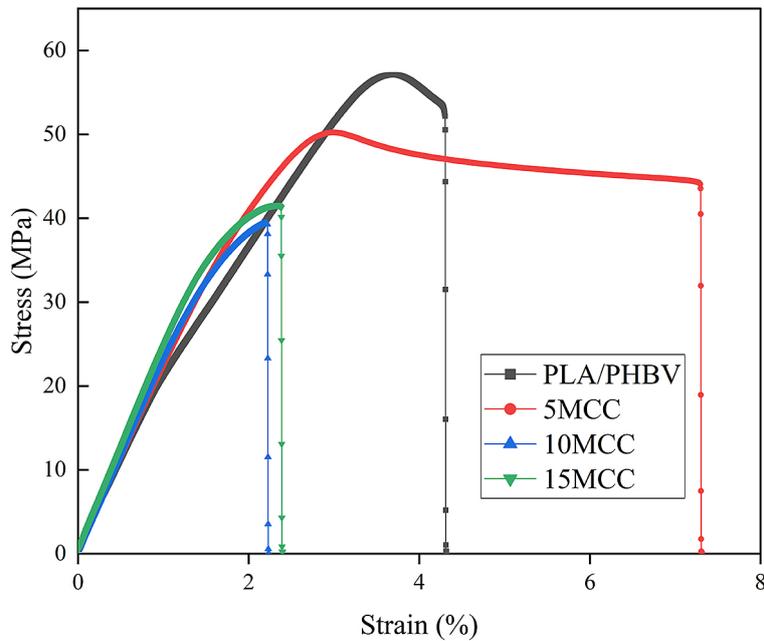


Figure 1. Example of stress-strain curves

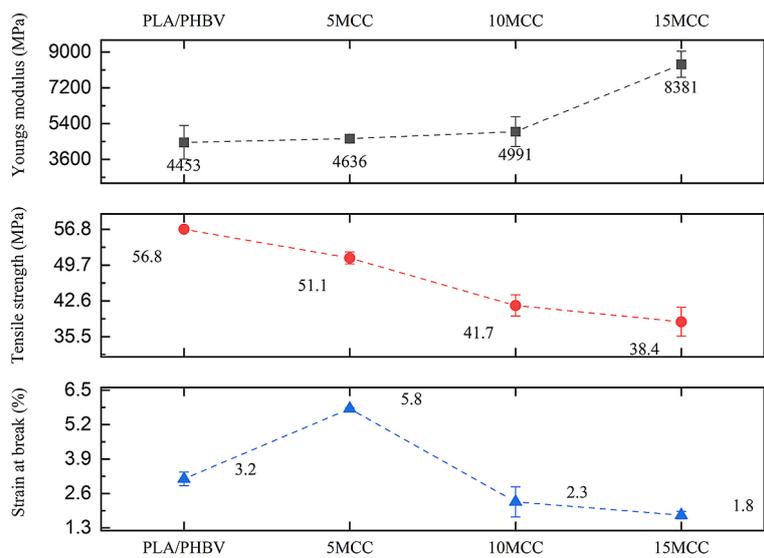


Figure 2. Comparison of tensile properties

increased, Young's modulus and flexural modulus increased, resulting in increased stiffness of the material. The decrease in strength with higher fiber content can be attributed to poor cellulose adhesion to the polymer matrix, and the microfibers themselves can introduce internal stresses that weaken the material.

The integration of cellulose into polymer composites significantly impacts their mechanical properties. However, other studies have demonstrated that enhancing the cellulose content in composites optimizes these properties, with the most favorable results achieved at specific

concentrations of cellulose [36]. The influence on the mechanical properties of polymer composites depends on the type of cellulose utilized and the modification techniques applied. For example, plasma- and TEMPO-modified celluloses have an effect on the morphology, thermal, and mechanical properties of poly(3-hydroxybutyrate) composites [37]. Cellulose nanofibers and similar fibers have been extensively studied as reinforcements for polymer nanocomposites, exhibiting exceptional mechanical and thermal properties [38]. The interfacial adhesion between cellulose and the polymer matrix plays a critical role in

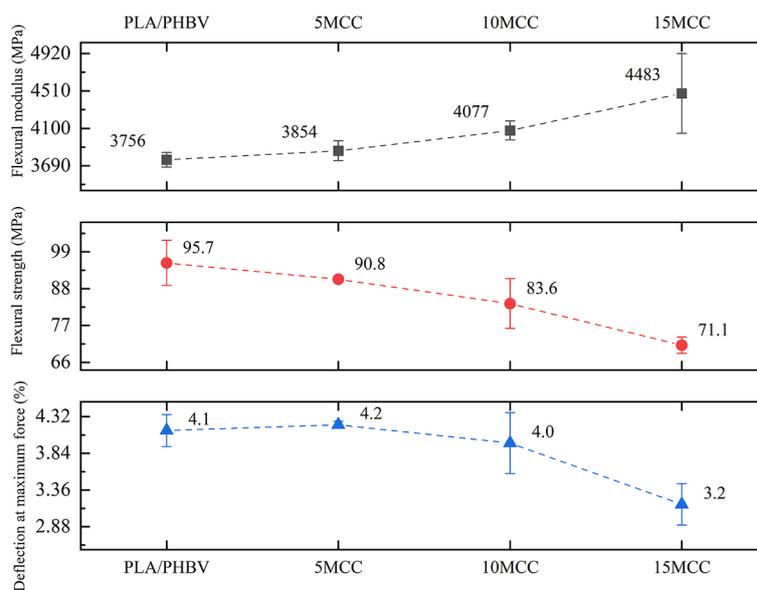


Figure 3. Comparison of flexural properties

enhancing these properties [39]. Moreover, the dispersion of cellulose nanofibers in polymer matrices results in a significant increase in tensile strength, highlighting cellulose’s positive effects reinforcement [40]. The mechanical properties of cellulose-based polymer composites can be further optimized by pre-fibrillation of the pulp, resulting in cellulosic nanofiber-reinforced polymers with excellent mechanical properties and a low coefficient of thermal expansion [41]. Additionally, microcrystalline cellulose as a reactive reinforcing filler has been shown to enhance the mechanical properties and thermal stability of polymer composites [42].

The incorporation of various forms of cellulose, including cellulose nanocrystals, fibers, and tendrils, into polymer composites has garnered significant attention from researchers [43–45]. These materials, derived from plants and bacteria, possess the potential to enhance the mechanical properties and moisture resistance of polymer composites [46, 47]. The primary motivation for using cellulose fibers in polymer composites is their environmental friendliness, stemming from the renewability of cellulose [48]. Studies have shown that cellulose nanocrystals and nanofibers have a synergistic effect on polymer nanocomposites [49]. The interaction between cellulose fibers and the polymer matrix is a critical factor influencing the overall performance of the composite material [42]. Moreover, cellulose has been demonstrated to improve the thermal stability of polymer composites [50]. Research has also investigated the

effects of cellulose fillers on various polymer matrices, such as polypropylene, epoxidized soybean oil, and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) concluding that the addition of cellulose increases their mechanical properties [50, 51]. Furthermore, studies have been conducted on the development of biodegradable polymer composites using cellulose fibers derived from various sources, such as hollow bunches of oil palm fruits. Surface modification of MCC constitutes a critical area of research aimed at enhancing the interfacial adhesion between MCCs and polymer matrices in composite materials. Augmenting this adhesion is essential for improving the mechanical properties and overall efficacy of polymer composites. Various surface modification strategies have been developed, each with its distinct mechanisms of action and effects.

One efficacious approach involves the utilization of chemical treatments to modify the surface properties of MCCs. For instance, silanization is frequently employed to enhance the compatibility of hydrophilic cellulose fibers with hydrophobic polymer matrices. This technique augments interfacial adhesion, thereby improving cellulose-polymer interactions, while concurrently reducing moisture absorption, resulting in enhanced mechanical properties [52]. Furthermore, the utilization of diblock copolymer dispersants enhances the wettability of cellulose nanofibers (CNFs) in polymer matrices, thereby reducing fiber-fiber interactions and improving fiber dispersion within the matrix [53]. An alternative promising approach

involves the grafting of polymers onto the surface of MCC, which alters its surface properties and enhances interaction with the polymer matrix. For instance, research conducted by Wang et al. demonstrated that grafting the polymer onto the surface of the MCC significantly increased the adhesion between the MCC and the polybutylene adipate-co-terephthalate (PBAT) matrix, resulting in enhanced mechanical properties of the composite [54]. Similarly, the utilization of adhesion peptides, inspired by mechanisms observed in nature, enhanced the adhesion strength at the MCC boundary, demonstrating the potential of biomimetic approaches for advanced materials design [44].

In addition to chemical modifications, physical methods such as steam blast treatment that enhance the mechanical properties of MCC-filled composites were also investigated. This process alters the structure of the cellulose, increasing its surface area and facilitating improved interaction with the polymer matrix [55]. The utilization of coupling agents has been demonstrated to enhance the thermal stability and mechanical properties of composites by augmenting the adhesion between cellulose fibers and the matrix [56].

In conclusion, MCC surface modification plays a crucial role in enhancing interfacial adhesion in polymer composites. Techniques such as chemical processing, polymer grafting, and physical modifications contribute to increased interfacial interactions, resulting in improved mechanical properties and enhanced performance of composites. Ongoing research in this field facilitates the development

of innovative methods to optimize the utilization of MCC in diverse polymer applications.

Thermal aging

The assessment of strength properties was repeated following the accelerated thermal aging process. The aging process has a significant impact on polymers and polymer composites, resulting in changes to their mechanical, rheological, and thermal properties [57]. This process may involve rapid compaction, gradual rearrangement of chains, brittleness due to internal stresses, and slow degradation of properties when exposed to external factors such as light, temperature, and humidity [58]. Aging can cause polymer chains to break, produce free radicals, and reduce molecular weight, leading to deterioration of material properties [59]. Environmental processes, such as photochemical weathering, can also alter the physicochemical properties of polymers, affecting their fate and transport. Furthermore, aging accelerates the degradation of polymers under thermal oxidation conditions, particularly when exposed to UV light [60, 61]. Aging can also affect chemical composition, rheological and mechanical properties, reduce gas permeability, and lead to other mechanical changes [62].

The outcomes of mechanical testing following the accelerated thermal aging process are depicted in Figure 4–5. The PLA/PHBV blend experienced complete degradation. In contrast, samples containing microcellulose were not fully

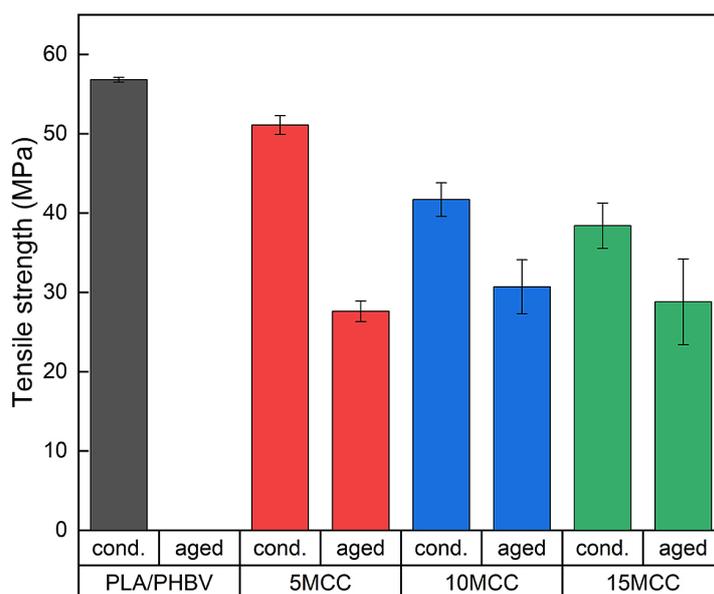


Figure 4. Comparison of tensile strength before and after accelerated thermal aging

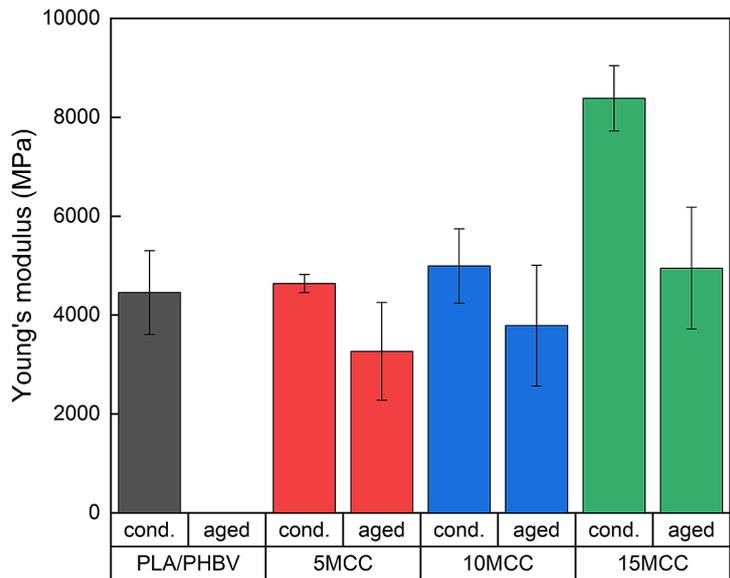


Figure 5. Comparison of Young's modulus before and after accelerated thermal aging

degraded, demonstrating the stabilizing influence of cellulose, which mitigates the impact of external factors. Both materials exhibited a decrease in mechanical properties compared to non-aged materials, with higher cellulose content correlating with increased resistance to aging agents. These findings align with those of Omar et al., who investigated the influence of microcellulose on a PLA/LLDPE composite subjected to accelerated aging. Their results indicated that composites containing microcellulose exhibited greater resistance to aging [63]. It is essential to emphasize the role of microcellulose in this type of biodegradable composites, as it suspends the stability of the material. However, with the use of appropriate environmental conditions, these materials will completely degrade without adverse effects on the natural environment. The high crystallinity of MCC is a critical factor in enhancing its resistance to environmental conditions. The crystal structure confers superior mechanical strength and thermal stability compared to amorphous forms, enabling the maintenance of integrity under varying conditions such as temperature and humidity fluctuations. Research has demonstrated that MCCs, when utilized as a filler in polymer matrices, enhance the thermal properties of composites, enabling them to withstand elevated temperatures without degradation [42].

Due to its low coefficient of thermal expansion, MCC exhibits dimensional stability, thereby reducing the risk of deformation and delamination in composites subjected to temperature and

humidity fluctuations. This characteristic enhances their overall thermal stability and performance in adverse environmental conditions [55, 64].

Results show that increased MCC content can have a stabilising effect, making an important contribution to the development of more durable biodegradable materials. However, the authors note that accelerated aging, used in the study as a method to simulate long-term environmental effects, does not fully reflect the actual conditions of natural aging. Accelerated aging tests involve the intensification of factors such as temperature, humidity or UV radiation, which accelerates degradation processes, but does not accurately reflect the variability and complexity of natural environments. As a result, the results obtained under such conditions may differ from observations in real-world applications, requiring caution in interpreting and transferring conclusions to practice. Highlighting this difference is crucial to gain a complete understanding of the behavior of materials in their actual life cycle.

Mechanical hysteresis loop

The concept of determining the initial mechanical hysteresis loops during cyclic loading and unloading tests is utilized to evaluate energy dissipation in materials. In conventional materials, energy is primarily dissipated through internal friction, whereas in composites, energy is additionally dissipated through interactions between the components, such as the detachment of reinforcement from the matrix. Cieszyński and

Topoliński’s research demonstrated that scattering energy analysis can assess the quality of processing and predict the long-term properties of composites. Variations in energy dissipation during the first few load cycles may indicate the interactions between the matrix and the reinforcement, as well as the occurrence of critical stress states in the interfacial areas, resulting in relaxation and cracking, which are visible as hysteresis loops [65, 66]. Figures 6–7 depict the outcomes of the initial 20 hysteresis loops, obtained in the material’s elastic range, with a maximum load of 1000 N.

The study’s outcomes revealed that the materials with 10% and 15% microcellulose additives had higher dissipation energy compared to the base material and the composite with 5% content. Conforming to the principles outlined by

Cieszynski and Porebska et al. [67,68], the energy dissipated in composites is used to counteract internal stresses. Incorporating an additive results in localized internal stresses, which are alleviated during the initial elastic load cycles. This concept is corroborated by the observation that the elastic modulus increased following the initial few load cycles and thereafter remained at a constant level. The findings of Mazur et al. [69] also provided a similar conclusion, indicating a decrease in dissipation energy during the initial load cycles.

Thermal and reological analysis

The thermal properties of manufactured composites were evaluated using differential scanning calorimetry (DSC) to determine the processing

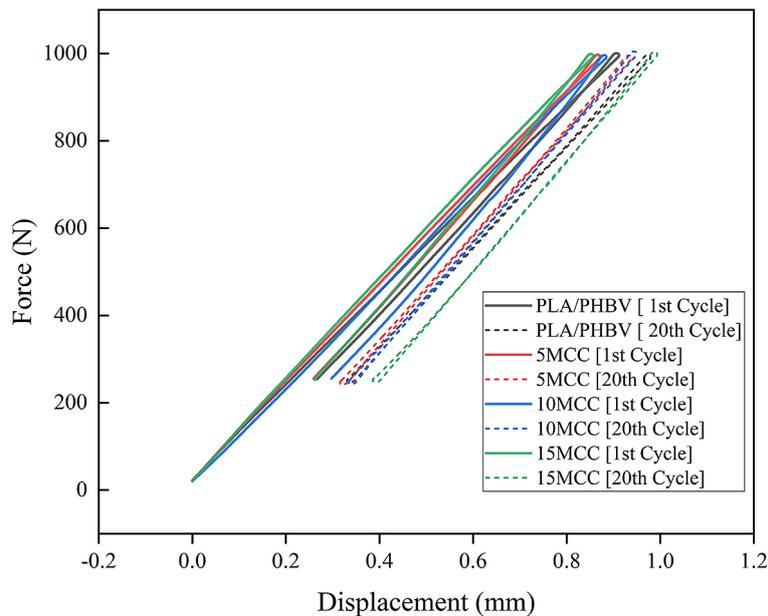


Figure 6. Comparison of the first and twentieth hysteresis loops

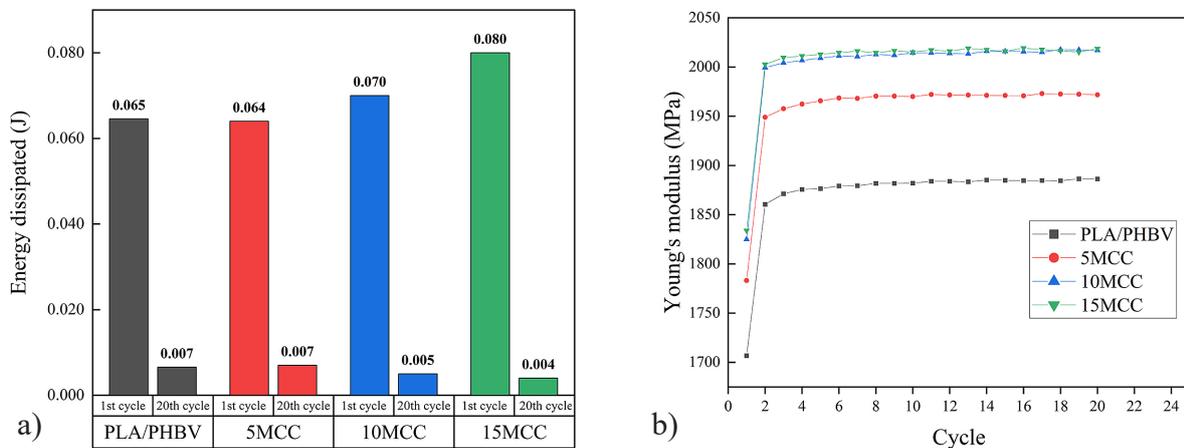


Figure 7. Comparison of dissipation energy (a) and Young’s modulus (b) in the first and twentieth load cycles

temperature ranges and the temperature of rheological properties measurements for the materials under consideration. The results of the DSC analysis are presented in Table 3, which lists the melting point at first heating (T_{m1}), the crystallization temperature (T_{cr}) and the melting enthalpy of the crystalline phase (ΔH_m). It is important to note that the filler used did not impact the crystal structure of the polymers.

Rheological properties are typically evaluated through the oscillatory rheometry method, which operates within small strain ranges and measures angular velocity up to 500 rad/s. These values can be related to results obtained through rotational or capillary rheometry. However, for composite materials containing filler particles that can be oriented in flow conditions, the above-mentioned combination may not be feasible. Nonetheless, the technique is useful for describing the relationships and interactions between components of multi-component polymer systems in the molten state. Rheological tests performed on materials based on PLA/PHBV demonstrated a significant impact of process conditions on rheological properties

(Figures 8–11). The combined viscosity values for the processed material were significantly reduced, and the addition of cellulose in amounts of 5% and 10% by weight further decreased the complex viscosity in the higher range of angular frequencies (Figures 8–9). However, a different trend was observed for the composite containing 15 wt.% of cellulose. For the batch containing the highest concentration of filler, only a decrease in viscosity values was observed across the entire range of angular frequencies, without the characteristic plateau seen in unmodified polymer and composites with lower filler content. The decrease in viscosity values observed for the PLA/PHBV sample in the range below 1 rad/s may be due to thermal or thermo-oxidative degradation of the polymer caused by the prolonged measurement time in an oxidizing atmosphere. Based on the tests conducted, it is suggested that the use of hydrolysis stabilizers or chain extenders may be necessary to increase the polymer's resistance to process conditions in the case of composites produced using PLA/PHBV. The addition of cellulose clearly resulted in a decrease in the viscosity of the composition, possibly

Table 3. DSC results

Designation	T_{m1} (°C)	T_{cr} (°C)	ΔH_m (J/g)
PLA/PHBV	170.4	119.1	125.2
5MCC	167.4	117.8	119.3
10MCC	168.5	117.7	117.0
15MCC	170.3	115.4	101.3

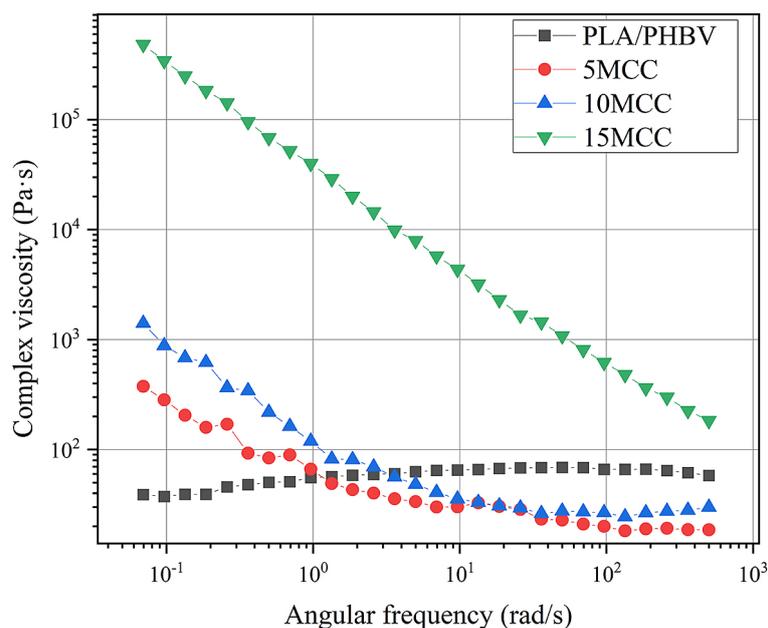


Figure 8. Complex viscosity of tested materials

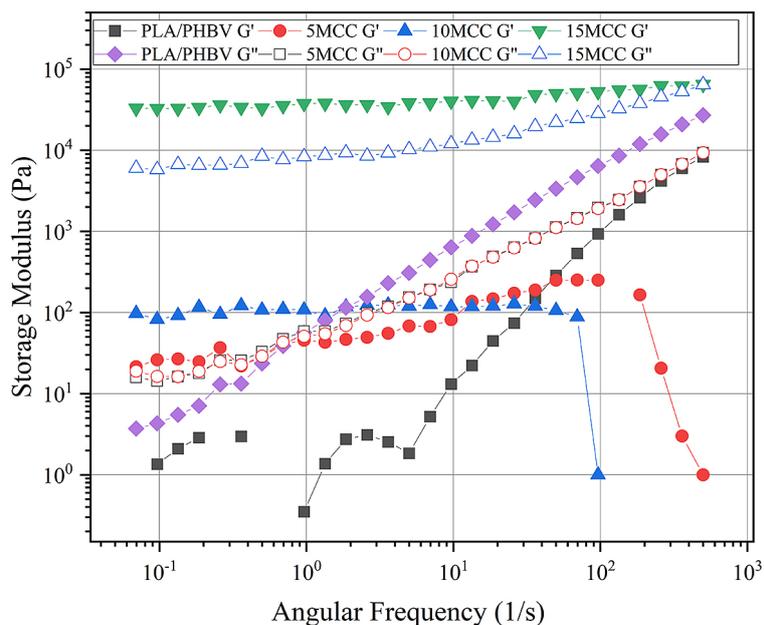


Figure 9. Storage modulus G' and loss modulus G'' for tested composites

due to degradation of the polymer matrix or the presence of pores, and the previously described increase in viscosity in the range of the lowest angular frequencies, likely caused by the formation of a structure of physically jammed filler particles in the alloy with limited mobility.

The rheological measurements obtained using a capillary rheometer were recorded in the form of data points, which displayed changes in unadjusted dynamic viscosity and shear stress according to fluctuations in shear rate. Although oscillatory rheometry is beneficial for examining interactions between composite elements, capillary rheometry is suitable for depicting flow conditions that are identical to those that occur during the extrusion process ($10\text{--}1,000\text{ s}^{-1}$) and injection ($100\text{--}100,000\text{ s}^{-1}$). Due to the particle size of the fillers and the concentrations used, a capillary nozzle with a diameter of 2 mm was required during the research, which restricted the capacity to attain high shear rates (maximum 900 s^{-1}). However, these rates are still relevant to the flow conditions in both technological processes. In rotational or oscillatory rheometry, it is common to observe significant differences in viscosity between material series containing fillers. For shear-thinned liquids, these disparities decrease as the shear rate increases, particularly in the case of capillary flow conditions. When in a molten state and subjected to the conditions used, all the polymer composites under consideration exhibited non-Newtonian shear-thinned liquid behavior. The formation of composites composed of

cellulose and PLA/PHBV was observed to be accompanied by unstable flow during measurement. This can be attributed to a higher volume fraction of the filler and probable cyclic blockage of the extruder nozzle. Flattening the flow curves in the range above 200 s^{-1} may be related to the transition to the second non-Newtonian flow range. From a processing standpoint, it is important to consider the limited control over the mold cavity filling process by adjusting parameters such as injection speed. However, increasing the shear rate is not expected to result in a significant decrease in the viscosity of the alloy (Figure 10–11).

The rheological properties was also examined using oscillatory and capillary rheometry methods, following a preliminary evaluation of the thermal properties. The use of differential scanning calorimetry enabled the determination of the melting point of individual polymers and composites, facilitating the selection of appropriate temperature settings for processing and measurements. This was particularly crucial, given that the proposed fillers were limited by the processing temperature range resulting from the incorporation of ingredients of natural origin (maximum temperature of $200\text{ }^{\circ}\text{C}$). The incorporation of cellulose into polymer composites has a significant effect on their rheological properties. Studies have demonstrated that cellulose increases viscosity and causes shear thinning of composite solutions, with this effect being more pronounced for cellulose than starch [70]. Furthermore, the

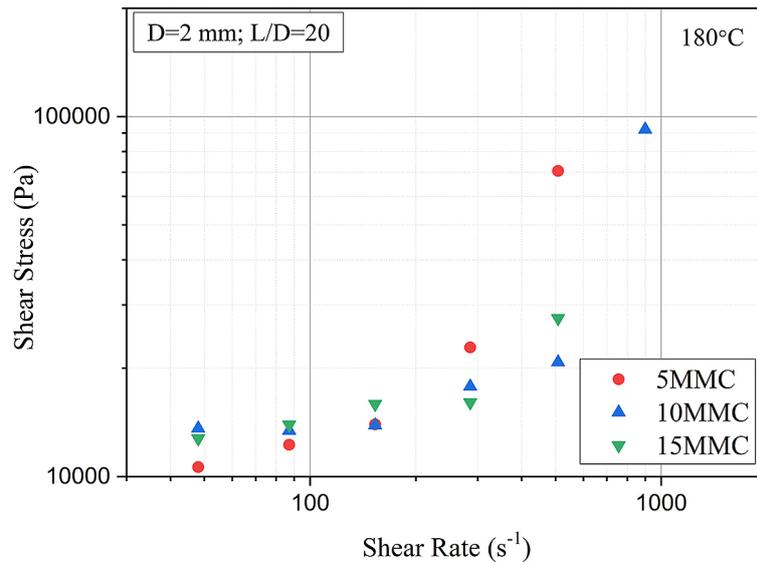


Figure 10. Shear stress of tested composites

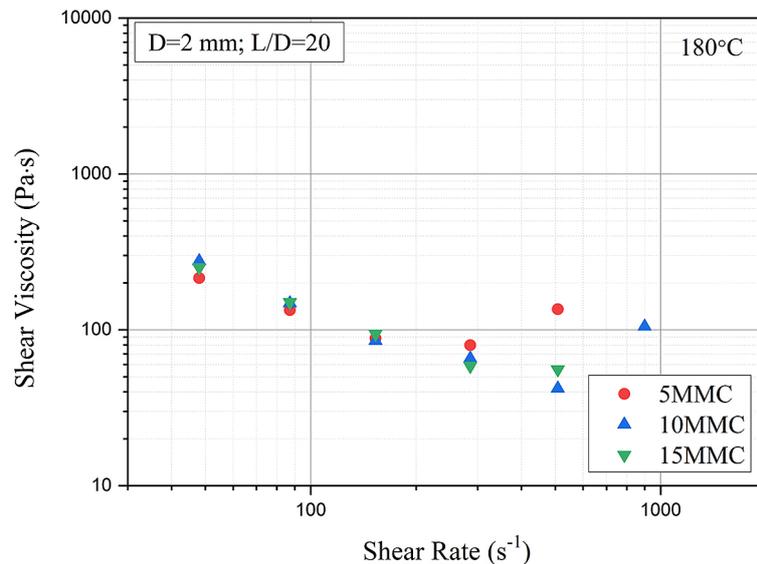


Figure 11. Shear viscosity of tested composites

initial length of cellulose fibers plays a vital role in shaping the rheological properties of composites, particularly at low fiber content levels. At higher fiber content levels, the amount of fiber content is the determining factor [71]. The addition of CNFs to polypropylene composites enhances the elastic modulus, complex viscosity, and transient shear stresses, while reducing creep deformation [72, 73]. The rheological behavior of cellulose nanocrystal suspensions is heavily influenced by the concentration and morphology of the nanoparticles, with a higher concentration of cellulose nanoparticles significantly impacting the rheological properties [74]. Enhancing the

processability of microcellulose in composites is crucial for improving their mechanical properties and expanding their applications. This enhancement can be achieved through chemical modifications, additives utilization, and processing conditions optimization. An exemplar of an efficacious method is the hybrid modification of microcellulose, which augments its hydrophobicity and compatibility with polymer matrices [75]. The incorporation of conductive polymers, such as polyaniline, enhances the conductivity, dispersion, and functionality of composites [76]. Optimization of techniques, such as sonication, enhances dispersion and interfacial bonding [77]. The utilization

of thermoplastic cellulose compounds and natural raw materials such as pineapple leaves facilitates the development of sustainable materials with enhanced properties [78]. The incorporation of maleic anhydride grafted polypropylene (MA-g-PP) as a compatibilizer enhances the adhesion between microcellulose and polypropylene, thereby increasing the mechanical strength of the composites. For instance, impact resistance exhibits an increase of 13% [79]. Compatibilizers such as MA-g-PP or itaconic acid copolymer enhance the adhesion between cellulose particles and the matrix by minimizing interfacial voids and improving dispersion [80]. Surfactants also enhance dispersion and mechanical properties, particularly in nanocellulose systems [81]. Optimization of fiber size and shape further enhances the efficiency of composites [82].

Morphological analysis

Microscopic observations were conducted on the fractures of composites after the static tensile test, and the results are depicted in Figures 12–15. The findings indicated that the addition of microcellulose caused the cracking to become

increasingly brittle. The microcellulose was uniformly dispersed within the polymer matrix. No evidence of the pulling out mechanism was found. The materials cracked at the filler-warp interface, and a decrease in tensile strength suggested poor adhesion to the matrix. However, the introduction of well-embedded particles affected the material's stiffness. Additionally, a large variance in the size of cellulose particles, ranging from 20 to 700 micrometers, was observed. The dispersion of MCC in polymer matrices significantly influences the mechanical properties of composites and the fiber-matrix interface. The uniform dispersion of MCC enhances interfacial adhesion, facilitating efficient stress transfer and improving mechanical properties due to the formation of hydrogen bonds between cellulose hydroxyl groups and polymer chains [83–87]. Insufficient dispersion, conversely, results in the agglomeration of MCC, thereby limiting the contact area with the matrix and consequently diminishing the adhesion and mechanical properties of the composite [88, 89]. The dimensions and morphology of MCC particles also play a crucial role – particles of smaller size provide a greater binding surface area, thereby enhancing their strengthening efficacy [90]. The utilization

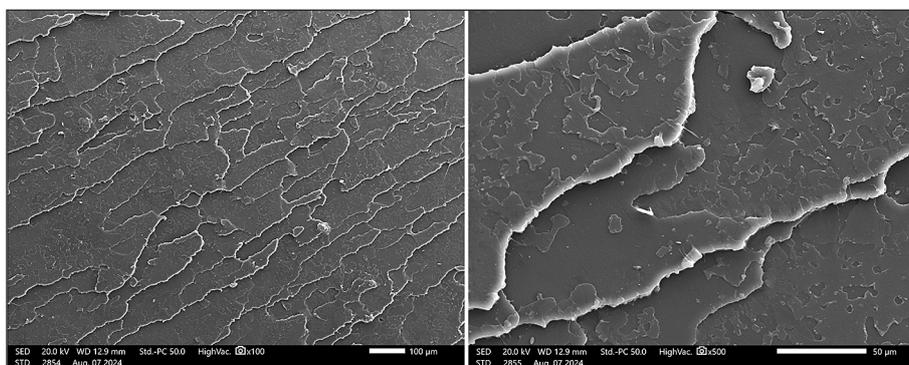


Figure 12. SEM images of PLA/PHBV material

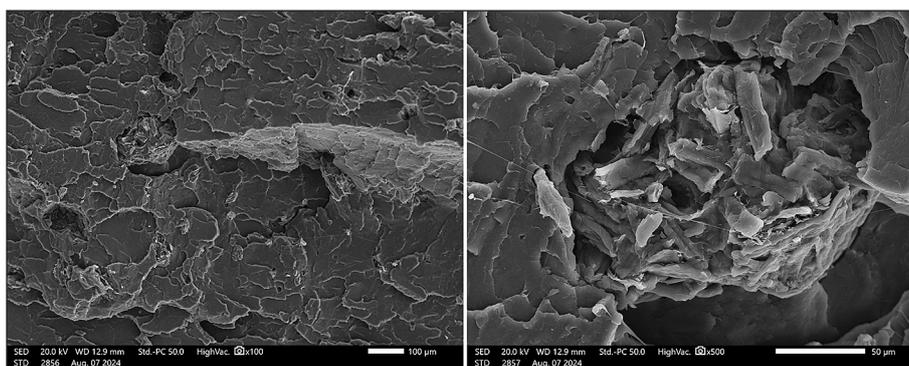


Figure 13. SEM images of PLA/PHBV modified with 5 wt.% of microcellulose

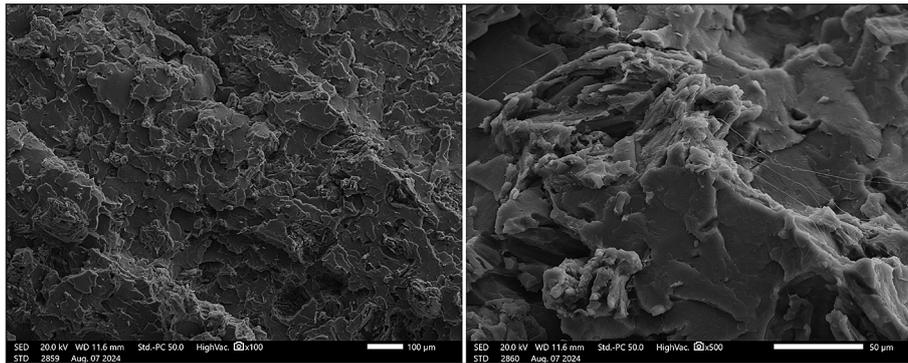


Figure 14. SEM images of PLA/ PHBV modified with 10 wt.% of microcellulose

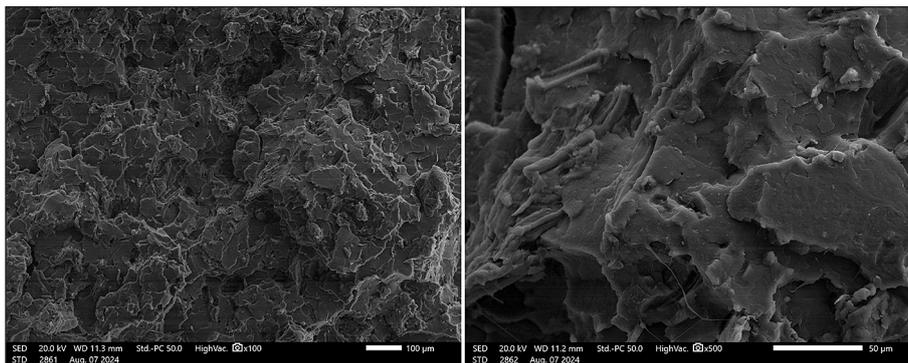


Figure 15. SEM images of PLA/ PHBV modified with 15 wt.% of microcellulose

of compatibilizers, such as maleic anhydride, enhances the dispersion of MCCs in hydrophobic polymer matrices, thereby improving the interfacial adhesion and mechanical properties of the resultant composites [91, 92]. This approach is particularly applicable to enhancing the compatibility of MCCs with hydrophobic polymers [93].

CONCLUSIONS

The research findings illustrate the favorable effect of incorporating microcellulose in biodegradable materials. The addition of cellulose particles enhances the stiffness and resistance of the material to aging agents. It is important to note that the concentration of the additive is a critical factor, and suspending it up to 15% by weight may cause processing difficulties. However, the ability to regulate the amount of additive and the property of the material by creating biodegradable polymer blend matrix composites with no negative environmental impact opens up numerous potential applications.

In addition, studies have shown that cellulose improves the mechanical properties of

natural fiber composites, such as sisal, flax, jute, and coconut fiber. These types of materials represent the future of composite materials and have a wide range of applications, and additionally they are harmless, renewable and have the required strength properties. MCC modified PLA and PHBV blends are innovative and significant for enhancing their mechanical properties such as tensile strength and elastic modulus. MCC enhances the biodegradability of these materials, expedites the degradation process, which is beneficial for the environment.

Furthermore, MCC reduces production expenses and minimizes the utilization of petrochemicals, contributing to more sustainable development. This modification also improves the thermal stability and barrier properties of the compounds. Extraction from waste, for example through enzymatic hydrolysis, is economically viable and environmentally sustainable. MCC-reinforced composites reduce the need for additional materials and have a longer service life, which lowers production costs. Thanks to its biodegradability, MCC supports sustainable products, which increases their market attractiveness and consumer value.

REFERENCES

- Djouina M, Loison S, Body-Malapel M. Recent progress in intestinal toxicity of microplastics and nanoplastics: systematic review of preclinical evidence. *Microplastics* 2024;3:217–33. <https://doi.org/10.3390/microplastics3020013>
- Ardusso M, Forero-López AD, Buzzi NS, Spetter CV, Fernández-Severini MD. COVID-19 pandemic repercussions on plastic and antiviral polymeric textile causing pollution on beaches and coasts of South America. *Science of the Total Environment* 2021;763:144365. <https://doi.org/10.1016/j.scitotenv.2020.144365>
- Soong YHV, Sobkowicz MJ, Xie D. Recent advances in biological recycling of polyethylene terephthalate (PET) plastic wastes. *Bioengineering* 2022;9:1–27. <https://doi.org/10.3390/bioengineering9030098>
- Álvarez M, Ferrández D, Zaragoza-Benzal A, Colorado-Pastor B. Initiative to increase the circularity of HDPE waste in the construction industry: A physico-mechanical characterization of new sustainable gypsum products. *Applied Sciences (Switzerland)* 2024;14. <https://doi.org/10.3390/app14020478>
- Bleszynski M, Clark E. Preliminary assessment into the prevalence and distribution of microplastics in north and south Pacific Island Beaches. *Microplastics* 2023;2:219–29. <https://doi.org/10.3390/microplastics2030018>
- Allen D, Allen S, Le Roux G, Simonneau A, Galop D, Phoenix VR. Temporal archive of atmospheric microplastic deposition presented in ombrotrophic Peat. *Environ Sci Technol Lett* 2021;8:954–60. <https://doi.org/10.1021/acs.estlett.1c00697>
- Wright SL, Kelly FJ. Plastic and human health: A micro issue? *Environ Sci Technol* 2017;51:6634–47. <https://doi.org/10.1021/acs.est.7b00423>
- El-Dash HA, Yousef NE, Aboelazm AA, Awan ZA, Yahya G, El-Ganiny AM. optimizing eco-friendly degradation of polyvinyl chloride (PVC) plastic using environmental strains of malassezia species and *Aspergillus fumigatus*. *Int J Mol Sci* 2023;24. <https://doi.org/10.3390/ijms242015452>
- Huda SN, Ramadhan MF. Designing educational game to increase environmental awareness. *International Journal of Emerging Technologies in Learning* 2021;16:181–93. <https://doi.org/10.3991/ijet.v16i15.22661>
- Wang Q, Zhang M, Li R. The COVID-19 pandemic reshapes the plastic pollution research – A comparative analysis of plastic pollution research before and during the pandemic. *Environ Res* 2022;208:112634. <https://doi.org/10.1016/J.ENVRES.2021.112634>
- van Emmerik T, de Lange S, Frings R, Schreyers L, Aalderink H, Leusink J, et al. Hydrology as a driver of floating river plastic transport. *Earths Future* 2022;10:1–20. <https://doi.org/10.1029/2022EF002811>
- Davoodi MN, Milani JM, Farahmandfar R. Preparation and characterization of a novel biodegradable film based on sulfated polysaccharide extracted from seaweed *Ulva intestinalis*. *Food Sci Nutr* 2021;9:4108–16. <https://doi.org/10.1002/fsn3.2370>
- Liu C, Liu C. Exploring plastic-management policy in china: status, challenges and policy insights. *Sustainability (Switzerland)* 2023;15. <https://doi.org/10.3390/su15119087>
- Patrício Silva AL, Prata JC, Walker TR, Duarte AC, Ouyang W, Barcelò D, et al. Increased plastic pollution due to COVID-19 pandemic: Challenges and recommendations. *Chemical Engineering Journal* 2021;405:126683. <https://doi.org/10.1016/j.cej.2020.126683>
- Marchelli F. Fostering bioplastics circularity through hydrothermal treatments: degradation behavior and products. *ACS Sustain Chem Eng* 2024;12:9257–67.
- Rosenboom JG, Langer R, Traverso G. Bioplastics for a circular economy. *Nat Rev Mater* 2022;7:117–37. <https://doi.org/10.1038/s41578-021-00407-8>
- Folino A, Karageorgiou A, Calabrò PS, Komilis D. Biodegradation of wasted bioplastics in natural and industrial environments: a review. *Sustainability (Switzerland)* 2020;12:1–37.
- Mangal M, Rao CV, Banerjee T. Bioplastic: an eco-friendly alternative to non-biodegradable plastic. *Polym Int* 2023;72:984–96. <https://doi.org/10.1002/pi.6555>
- Joo SH. Addressing climate change mitigation: Implications for the sustainable alternatives to plastics. *Cambridge Prisms: Plastics* 2024;2:1–10. <https://doi.org/10.1017/plc.2024.1>
- Zielińska M, Bułkowska K. Agricultural wastes and their by-products for the energy market. *Energies (Basel)* 2024;17. <https://doi.org/10.3390/en17092099>
- Bean SR, Ioerger BP, Park SH, Singh H. Interaction between sorghum protein extraction and precipitation conditions on yield, purity, and composition of purified protein fractions. *Cereal Chem* 2006;83:99–107. <https://doi.org/10.1094/CC-83-0099>
- Ncube A, Mtetwa S, Bukhari M, Fiorentino G, Passaro R. circular economy and green chemistry: The need for radical innovative approaches in the design for new products. *Energies (Basel)* 2023;16:1–21. <https://doi.org/10.3390/en16041752>
- Farghali M, Mohamed IMA, Osman AI, Rooney DW. Seaweed for climate mitigation, wastewater treatment, bioenergy, bioplastic, biochar, food, pharmaceuticals, and cosmetics: a review. vol. 21. Springer International Publishing; 2023. <https://doi.org/10.1007/s10311-022-01520-y>
- Matthew C, Bche C, Engineering C. Development of bio-derived and biodegradable polyhydroxyalkanoate (PHA)-based wood plastic composites (WPCs) 1968.

25. Vach Agocsova S, Culenova M, Birova I, Omanikova L, Moncmanova B, Danisovic L, et al. Resorbable biomaterials used for 3D scaffolds in tissue engineering: A review. *Materials* 2023;16. <https://doi.org/10.3390/ma16124267>
26. Jost V, Kopitzky R. Blending of polyhydroxybutyrate-co-valerate with polylactic acid for packaging applications – Reflections on miscibility and effects on the mechanical and barrier properties. *Chem Biochem Eng Q* 2015;29:221–46. <https://doi.org/10.15255/CABEQ.2014.2257>
27. Kim HS, Chen J, Wu LP, Wu J, Xiang H, Leong KW, et al. Prevention of excessive scar formation using nanofibrous meshes made of biodegradable elastomer poly(3-hydroxybutyrate-co-3-hydroxyvalerate). *J Tissue Eng* 2020;11. <https://doi.org/10.1177/2041731420949332>
28. Khamplod T, Winterburn JB, Cartmell SH. Electrospun poly(3-hydroxybutyrate-co-3-hydroxyvalerate) scaffolds—a step towards ligament repair applications. *Sci Technol Adv Mater* 2022;23:895–910. <https://doi.org/10.1080/14686996.2022.2149034>
29. Amaro L, Correia DM, Marques-Almeida T, Martins PM, Pérez L, Vilas JL, et al. Tailored biodegradable and electroactive poly(Hydroxybutyrate-co-hydroxyvalerate) based morphologies for tissue engineering applications. *Int J Mol Sci* 2018;19. <https://doi.org/10.3390/ijms19082149>
30. Chen W, Li Y, Huang Y, Dai Y, Xi T, Zhou Z, et al. Quercetin modified electrospun PHBV fibrous scaffold enhances cartilage regeneration. *J Mater Sci Mater Med* 2021;32. <https://doi.org/10.1007/s10856-021-06565-z>
31. Krikštanavičiene K, Stanys S, Jonaitiene V. Comparative investigation of mechanical-physical characteristics of biodegradable and non-degradable yarns. *Autex Research Journal* 2014;14:61–72. <https://doi.org/10.2478/aut-2014-0001>
32. Zhao X, Anwar I, Zhang X, Pellicciotti A, Storts S, Nagib DA, et al. Thermal and barrier characterizations of cellulose esters with variable side-chain lengths and their effect on PHBV and PLA bioplastic film properties. *ACS Omega* 2021;6:24700–8. <https://doi.org/10.1021/acsomega.1c03446>
33. González-Ausejo J, Sánchez-Safont E, Lagarón J, Balart R, Cabedo L, Gámez-Pérez J. Compatibilization of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)–poly(lactic acid) blends with diisocyanates. *J Appl Polym Sci* 2017;134:44806. <https://doi.org/10.1002/app.44806>
34. Valle Iulianelli GC, Costa LV, da Silva PSC, dos Santos FA. Evaluation of fully biodegradable PLA/PHB blend filled with microcrystalline celluloses. *Materials Research* 2023;26:16–8. <https://doi.org/10.1590/1980-5373-MR-2022-0433>
35. Badura K. Effect of nano and micro size of copper oxide on the properties of thermoplastic elastomer. *Advances in Science and Technology Research Journal* 2024;18(7); 78-91.
36. Uto K, Liu Y, Mu M, Yamamoto R, Azechi C, Tenjimbayashi M, et al. Humidity-responsive polyvinyl alcohol/microcrystalline cellulose composites with shape memory features for hair-styling applications. *Adv Mater Interfaces* 2024;11. <https://doi.org/10.1002/admi.202300274>
37. Celluloses T, Panaitescu DM, Vizireanu S, Stoian SA, Nicolae C, Gabor AR, et al. Poly (3-hydroxybutyrate) Modified by Plasma and n.d.:1–16.
38. Boujemaoui A, Ansari F, Berglund LA. Nanostructural effects in high cellulose content thermoplastic nanocomposites with a covalently grafted cellulose-poly(methyl methacrylate) interface. *Biomacromolecules* 2019; 20: 598–607. <https://doi.org/10.1021/acs.biomac.8b00701>
39. Ren Z, Guo R, Bi H, Jia X, Xu M, Cai L. Interfacial adhesion of polylactic acid on cellulose surface: A molecular dynamics study, 2020. <https://doi.org/10.1021/acssami.9b20101>
40. Wang B, Sain M. Dispersion of soybean stock-based nanofiber in plastic matrix. *ACS Symposium Series*, 2006;938:187–208. <https://doi.org/10.1021/bk-2006-0938.ch013>
41. Igarashi Y, Sato A, Okumura H, Nakatsubo F, Kuboki T, Yano H. Pre-fibrillation of pulps to manufacture cellulose nano ber reinforced high-density polyethylene using the dry-pulp direct kneading method. *Cellulose*, 2022: 1–21.
42. He M, Zhou J, Zhang H, Luo Z, Yao J. Microcrystalline cellulose as reactive reinforcing fillers for epoxidized soybean oil. *Polymer Composites* 2015;42488:6–13. <https://doi.org/10.1002/app.42488>
43. Barkane A. Cellulose nanocrystals vs. cellulose nanofibers: A comparative study of reinforcing effects in uv-cured vegetable oil. *Nanocomposites* 2021.
44. Samyn P. Design of Cellulose Interfaces through Self-Assembly of Adhesive Peptides with Intrinsic Stress Sensitive Properties, 2021:32. <https://doi.org/10.3390/cgpm2020-07157>
45. Hosoda N, Tsujimoto T, Uyama H. Green Composite of Poly(3-hydroxybutyrate- co -3- hydroxyhexanoate) Reinforced with Porous Cellulose 2014.
46. Myllytie P, Salmén L, Haimi E, Laine J. Viscoelasticity and water plasticization of polymer-cellulose composite films and paper sheets. *Cellulose* 2010;17:375–85. <https://doi.org/10.1007/s10570-009-9376-z>
47. Sain S, Ray D, Mukhopadhyay A. Improved mechanical and moisture resistance property of in situ polymerized transparent PMMA. *Cellulose Composites* 2014:1–11. <https://doi.org/10.1002/pc>
48. Oliveira P, Alexandre J, Gouveia RF, Strauss M. exploring the hierarchical structure and alignment of wood cellulose fibers for bioinspired anisotropic polymeric composites. *ACS Applied Bio Materials* 2020, 3(4). <https://doi.org/10.1021/acsabm.0c00038>

49. Jang SY, Kim DS. Physical properties of polypropylene composites with hydrophobized cellulose powder by soybean oil 2016;42929:1–8. <https://doi.org/10.1002/app.42929>
50. E. K. Silviya, G. Unnikrishnan, S. Varghese JTG. Thermal and mechanical characterization of EVA/Banana fiber-derived cellulose composites. *J Appl Polym Sci* 2012; 125: 786–792. <https://doi.org/10.1002/app>
51. Indrayani Y, Suryanegara L, Sagiman S, Roslinda E, Marwanto M. Biodegradable of bio-composites made from polylactid acid (PLA) and cellulose fibers from oil palm empty fruit bunch. *Nusantara Bioscience* 2019;11:8–11. <https://doi.org/10.13057/nusbiosci/n110102>
52. Calabria BP, Ninomiya F, Yagi H, Oishi A, Taguchi K, Kunioka M, et al. Biodegradable poly(butylene succinate) composites reinforced by cotton fiber with silane coupling agent. *Polymers (Basel)* 2013;5:128–41. <https://doi.org/10.3390/polym5010128>
53. Sakakibara K, Moriki Y, Yano H, Tsujii Y. Strategy for the improvement of the mechanical properties of cellulose nanofiber-reinforced high-density polyethylene nanocomposites using diblock copolymer dispersants. *ACS Appl Mater Interfaces* 2017;9:44079–87. <https://doi.org/10.1021/acsami.7b13963>
54. Wang H, Liu X, Liu J, Wu M, Huang Y. Tailoring Interfacial Adhesion between PBAT Matrix and PTFE-Modified Microcrystalline Cellulose Additive for Advanced Composites. *Polymers (Basel)* 2022;14. <https://doi.org/10.3390/polym14101973>
55. Tienne LGP, Cordeiro S., Brito EB, Marques MFV. Microcrystalline cellulose treated by steam explosion and used for thermo-mechanical improvement of polypropylene. *J Compos Mater* 2020;54:3611–24. <https://doi.org/doi:10.1177/0021998320918645>
56. Mahmoud Y, Safidine Z, Belhaneche-Bensemra N. Characterization of microcrystalline cellulose extracted from walnut and apricots shells by alkaline treatment. *Journal of the Serbian Chemical Society* 2021;86:521–32. <https://doi.org/10.2298/JSC200806011M>
57. Smith SJD, Hou R, Konstas K, Akram A, Lau CH, Hill MR. Control of physical aging in super-glassy polymer mixed matrix membranes. *Acc Chem Res* 2020;53:1381–8. <https://doi.org/10.1021/acs.accounts.0c00256>
58. Akishev YS, Grushin ME, Drachev AI, Karalnik VB, Petryakov A V, Trushkin NI. On hydrophilicity ageing of PP and PET films induced by ultraviolet radiation and hydrogen atoms. *The Open Plasma Physics Journal*, 2013; 6: 19–29.
59. Wang B, Zhao K, Zhang Y, Tao Y, Zhou X, Song L. Influence of aging conditions on the mechanical properties and flame retardancy of HIPS composites 2018;46339:1–9. <https://doi.org/10.1002/app.46339>
60. Schefer RB, Armanious A, Mitrano DM. Eco-corona formation on plastics: adsorption of dissolved organic matter to pristine and photochemically weathered polymer surfaces. *Environ Sci Technol* 2023; 57: 14707–16. <https://doi.org/10.1021/acs.est.3c04180>
61. Maraveas C, Kyrtopoulos IV, Arvanitis KG, Bartzanas T. The aging of polymers under electromagnetic radiation. *Polymers (Basel)* 2024;16. <https://doi.org/10.3390/polym16050689>
62. Yin H, Chapala P, Bermeshev M, Schönhals A, Böhnig M. Molecular mobility and physical aging of a highly permeable glassy polynorborene as revealed by dielectric spectroscopy. *ACS Macro Lett* 2017; 6: 813–8. <https://doi.org/10.1021/acsmacrolett.7b00456>
63. Omran AAB, Mohammed AABA, Sapuan SM, Ilyas RA, Asyraf MRM, Kooloor SSR, et al. Micro- and nanocellulose in polymer composite materials: A review. *Polymers (Basel)* 2021;13:1–30. <https://doi.org/10.3390/polym13020231>
64. Ozen E, Yildirim N, Dalkilic B, Ergun ME. Effects of microcrystalline cellulose on some performance properties of chitosan aerogels. *Maderas: Ciencia y Tecnologia* 2021; 23: 1–10. <https://doi.org/10.4067/S0718-221X2021000100426>
65. Cieszyński T, Topoliński T. Badania zmęczeniowe kompozytów polimerowych przy sterowaniu energią dyssypacji. *Czasopismo Techniczne Mechanika -WPK Mechanika* 2006; 103: 115–9.
66. Mazurkiewicz S, Porębska R. Energia dyssypacji w kompozytach polimerowych. *Czasopismo Techniczne Mechanika -WPK* 2009; 106: 245–8.
67. Cieszyński T, Topoliński T. Badania zmęczeniowe kompozytów polimerowych przy sterowaniu energią dyssypacji. *Czasopismo Techniczne Mechanika -WPK Mechanika* 2006; 103: 115–9.
68. Mazurkiewicz S, Porębska R. Energia dyssypacji w kompozytach polimerowych. *Czasopismo Techniczne Mechanika -WPK* 2009; 106: 245–8.
69. Bazan P, Mazur KE, Rybicka K, Kuciel S. The influence of organic and inorganic antibacterial additives on the strength and biocidal properties of thermoplastic elastomers (TPO). *Industrial Crops & Products*, 2023; 198. <https://doi.org/10.1016/j.indcrop.2023.116682>
70. Shang X, Jiang H, Wang Q, Liu P, Xie F. Cellulose-starch Hybrid Films Plasticized by Aqueous ZnCl₂ Solution n.d. <https://doi.org/10.3390/ijms20030474>
71. Zhang DW, Li YJ, Feng YH, Qu JP, He HZ, Xu BP. Effect of initial fiber length on the rheological properties of sisal fiber/polylactic acid composites. *Polymer composites* 2011; 32(8): 1218-1224. <https://doi.org/10.1002/pc>
72. Wang L, Gardner DJ, Bousfield DW. Cellulose nanofibril-reinforced polypropylene composites for material extrusion: Rheological properties. *Polymer Engineering & Science*, 2018; 58(5): 793-801. <https://doi.org/10.1002/pen>
73. Bilcati GK, Costa M do R de M da, Tamura SHL da S. Effect of combined fiber-microcrystalline cellulose

- reinforcement on the rheology and hydration kinetics of cementitious composites. *Revista IBRACON de Estruturas e Materiais* 2024;17:1–17. <https://doi.org/10.1590/s1983-41952024000600004>
74. Zhou L, He H, Li M, Song K, Cheng HN, Wu Q. Morphological influence of cellulose nanoparticles (CNs) from cottonseed hulls on rheological properties of polyvinyl alcohol/CN suspensions. *Carbohydr Polym* 2016. <https://doi.org/10.1016/j.carbpol.2016.07.119>
 75. Yuan Q, Zhang G, Li C, Xu S, He L. Effect of amino silicone oil-phosphorylation hybrid modification on the properties of microcellulose fibers. *Polymers (Basel)* 2024;16. <https://doi.org/10.3390/polym16081123>
 76. Yuningsih LM, Mulyadi D, Indriani D. Synthesis of polyaniline microcellulose composite. *Jurnal Kimia Dan Kemasan* 2021;43:50. <https://doi.org/10.24817/jkk.v43i1.6326>
 77. Sitorus B, Pranata D, Bara'allo Malino M. Effect of sonication on the properties of composite polypyrrole/microcellulose and its potential as a capacitor. *Jurnal Kimia Riset* 2022;7:101–11. <https://doi.org/10.20473/jkr.v7i2.39416>
 78. Morales-Zamudio L, López-Marure A, García-Hernández M, Rodríguez-González F, Flores-Gallardo S, López-Martínez E. Isolation, characterization, and incorporation of microfibrils and microcrystals from *Typha domingensis* Pers. As impact strength reinforcer of polypropylene matrix composite using stearic acid as interfacial modifier. *Bioresources* 2019;14:2513–35. <https://doi.org/10.15376/biores.14.2.2513-2535>
 79. Sergi C, Sbardella F, Lilli M, Tirillò J, Calzolari A, Sarasini F. Hybrid cellulose–Basalt polypropylene composites with enhanced compatibility: The role of coupling agent. *Molecules* 2020;25. <https://doi.org/10.3390/molecules25194384>
 80. Gomez-Caturla J, Balart R, Ivorra-Martinez J, Garcia-Garcia D, Dominici F, Puglia D, et al. Biopolypropylene-based wood plastic composites reinforced with mango peel flour and compatibilized with an environmentally friendly copolymer from itaconic acid. *ACS Appl Polym Mater* 2022;4:4398–410. <https://doi.org/10.1021/acsapm.2c00373>
 81. Immonen K, Lahtinen P, Pere J. Effects of surfactants on the preparation of nanocellulose-PLA composites. *Bioengineering* 2017;4:1–13. <https://doi.org/10.3390/bioengineering4040091>
 82. Phomrak S, Nimpaboon A, Newby BMZ, Phisalaphong M. Natural rubber latex foam reinforced with micro- and nanofibrillated cellulose via dunlop method. *Polymers (Basel)* 2020;12:1–16. <https://doi.org/10.3390/polym12091959>
 83. Naduparambath S, Sreejith MP, Jinitha TV, Shaniba V, Aparna KB, Purushothaman E. Development of green composites of poly (vinyl alcohol) reinforced with microcrystalline cellulose derived from sago seed shells. *Polym Compos* 2018;39:3033–9. <https://doi.org/10.1002/pc.24307>
 84. Ong TK, Tshai KY, Choo HL, Khiew PS, Chung SL. Mechanical performance and biodegradability of polyvinyl alcohol nanocomposite films. *Materwiss Werksttech* 2020;51:740–9. <https://doi.org/10.1002/mawe.202000030>
 85. Karpiński R, Szabelski J, Krakowski P, Jonak J, Falkowicz K, Jojczuk M, et al. Effect of various admixtures on selected mechanical properties of medium viscosity bone cements: Part 1 – α/β tricalcium phosphate (TCP). *Compos Struct* 2024;343:118306. <https://doi.org/10.1016/j.compstruct.2024.118306>
 86. Karpiński R, Szabelski J, Krakowski P, Jonak J, Falkowicz K, Jojczuk M, et al. Effect of various admixtures on selected mechanical properties of medium viscosity bone cements: Part 2 – Hydroxyapatite. *Compos Struct* 2024;343:118308. <https://doi.org/10.1016/j.compstruct.2024.118308>
 87. Karpiński R, Szabelski J, Krakowski P, Jonak J, Falkowicz K, Jojczuk M, et al. Effect of various admixtures on selected mechanical properties of medium viscosity bone cements: Part 3 – Glassy carbon. *Compos Struct* 2024;343:118307. <https://doi.org/10.1016/j.compstruct.2024.118307>
 88. Wang Q, Ji C, Sun J, Zhu Q, Liu J. Structure and properties of polylactic acid biocomposite films reinforced with cellulose nanofibrils. *Molecules* 2020;25. <https://doi.org/10.3390/molecules25143306>
 89. Zhang Y, Liao H, Zhang Y, Zhang Y. Simultaneously enhancing microelastic response and degradability for poly(butylene succinate) composite monofilaments by silanized microcrystalline cellulose. *Cellulose* 2024;31:5591–608. <https://doi.org/10.1007/s10570-024-05940-7>
 90. Mahmoud Y, Belhanché-Bensemra N, Safidine Z. Impact of microcrystalline cellulose extracted from walnut and apricots shells on the biodegradability of Poly (lactic acid). *Front Mater* 2022;9:1–16. <https://doi.org/10.3389/fmats.2022.1005387>
 91. Shah P. Advancement in packaging film using microcrystalline cellulose and TiO₂. *American Journal of Polymer Science and Technology* 2017;3:97. <https://doi.org/10.11648/j.ajpst.20170306.11>
 92. Chen D, Huang B, Wang Z, Zheng Z, Li Z, Zhou H, et al. Development and molecular dynamics simulation of green natural rubber composites with modified sisal microcrystalline cellulose. *Journal of Vinyl and Additive Technology* 2023;29:294–310. <https://doi.org/10.1002/vnl.21964>
 93. Abdel Rahim M, Ismail M, Kandil A. Effect of organophilization and interlamellar silylation of montmorillonite on compatibilization of polymer composites. *Advances in Science and Technology Research Journal* 2016;10:206–16. <https://doi.org/10.12913/22998624/65121>