

Investigation on Tensile Properties of Polylactide-Nanoclay (PLA/ MMT) Surface Modification Nanocomposites

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ABSTRACT

Poly(lactic acid) (PLA) has gained significant attention as an environmentally friendly biopolymer, but its limited mechanical properties have hindered broader applications. Nanoparticles such as montmorillonite (MMT) offer a promising approach to address this limitation. The intercalation of MMT with polymer chains can significantly impact the mechanical properties of the nanocomposites. Hence, this paper investigated the effect of surface-modified montmorillonite (MMT) nanoparticles on the mechanical properties of poly(lactic acid) (PLA) nanocomposites. The acetylation process of MMT was carried out followed by neutralisation process with NaOH. PLA granules and acetylated-modified MMT were mixed, crushed into granular form, and moulded. The effect of varying concentrations of modified MMTs on the tensile strength, elongation at break, and maximum force of PLA/MMT nanocomposites was evaluated using the ASTM D638 standard. FTIR results showed shifts in peak intensities in regions 2750 cm^{-1} - 2810 cm^{-1} led to changes in the aliphatic and aromatic regions, which confirmed the presence of acetylation. Controlled surface modification improved interfacial interactions and load distribution, enhancing overall mechanical performance. The incorporation of surface-modified MMT in PLA/MMT nanocomposite increased the maximum force, Young's modulus, elongation at breaks and tensile strength. PLA/1wt% MMT and the PLA/7wt% MMT compositions exhibited good mechanical properties. However, the PLA/5 wt% MMT blend

is deemed more suitable for food applications, such as disposable cups, plates, and cutlery, due to its lower elongation point. In conclusion, the hydrophilic properties of MMT and the hydrophobic properties of PLA are compatible due to the synergistic effects during surface modification which enhance the overall performance of the nanocomposites.

Keywords: *Surface Modification; Polylactide Acid; Montmorillonite; Nanocomposite; Biodegradable*

Introduction

Plastics are made from petroleum-based materials that are not biodegradable and harmful to the environment. The process to dispose of petroleum-based plastics concerns the effect it has on the environment and its sustainability [1]-[3]. Hence, there have been continuous efforts and developments for producing biodegradable alternatives for plastic. Polylactic acid (PLA), a bio-based polymer, is an appropriate substitute when it comes to packaging materials since it offers standout qualities, including processability, biocompatibility and environmentally friendly.

However, due to its high cost, poor flexibility, hydrophobicity and slower degradation rate, PLA only has a limited number of uses in packaging materials, such as films, bags and containers [4]-[5]. It has been discovered in certain research that altering PLA by combining it with low-cost fillers (fillers) can assist in lowering its high cost and boost its performance [6]-[8].

Durable products made from PLA should be designed to achieve an extended service life, finding a harmonious equilibrium between environmental sustainability and optimal product performance, particularly for high-performance engineering applications. Recent advancements in enhancing the durability of PLA-based products involve the integration of hybrid carbon sources, combining non-renewable and renewable elements. This has been achieved through the incorporation of synthetic plastics, synthetic fibres, such as glass and carbon, natural fibres, and other biodegradable fillers [9].

Montmorillonite (MMT) is a highly soft phyllosilicate family of minerals and develops when minute crystals of clay precipitate from an aqueous solution. Over the last decade, there have been promising and intensive studies done for MMT as a partial replacement for petroleum-based plastics [10]. Several studies have reported the successful acetylation of montmorillonite by using different acylating agents, such as acetic anhydride, acetyl chloride and acetic acid. The acetylated montmorillonite has been found to exhibit improved thermal stability, hydrophobicity and mechanical properties, making it suitable for various applications [11].

The combination of nanoclays and active agents in nanocomposite films results in a material with enhanced mechanical strength, improved barrier properties, superior thermal characteristics, and notable antimicrobial efficacy, making it particularly suitable for applications where these properties are crucial, such as in food packaging and preservation [12].

Since PLA is hydrophobic and MMT being hydrophilic, it results in incompatibility. By using a proper surface modification in the MMT can improve its mechanical properties [12]. The main concern is how much MMT is to be added into the blend respectively, under a certain set of process parameters, for the best outcome that is fully biodegradable. The high percentage of MMT added to the blend restricts its mechanical applications and may cause brittleness [13].

Hence, this research focused on the investigation of acetylation surface modification of MMT and to produce an optimum blending process parameters and analysing the effect of blending towards the mechanical and morphological properties of PLA/MMT reinforced polymer composite. The optimum blending process parameter will help in producing PLA-based disposable cups, plates and cutlery in the food packaging industry. These items provided a sustainable alternative to conventional plastic disposables, especially for single-use applications in restaurants, cafeterias and events.

Methodology

Poly lactide acid (PLA) was supplied by Nature Works LLC, United States. Montmorillonite, (MMT) in the form of fine powder was supplied by Sigma Alrich. Hydrochloric acid, (HCL) was supplied from MERCK, Malaysia.

The MMT powder was oven dried for 6 hours at a temperature of 60 °C to remove any moisture content. Dried MMT powder of 50 g was placed in a cylindrical beaker where 500 mL, 1M of HCL acid was added. Then, the beaker containing the solution was placed on a magnetic stirrer. The temperature was kept at 40 °C and monitored throughout the process with a thermometer. The duration for this acetylation process was 2 hours.

Then, the MMT powder was continuously washed and filtered with distilled water till its pH level reached pH 7. To aid this neutralisation process, 5 mL, 1 M of NaOH was added to the solution. The modified MMT was then oven dried at 70 °C for 24 hours to remove any excess moisture. The modified MMT and PLA granules were mixed in a Sigma blade mixer with the formulation as highlighted in Table 1. The mixer was preheated to 80 °C. PLA granules were added followed by modified MMT powder. The PLA/MMT composite was mixed until it reached a homogeneous point which took about 20 minutes - 30 minutes. The PLA/MMT composite was then crushed into granular form with a blender.

The PLA/MMT composite was then moulded by using a hydraulic press at 500 PSI with the following parameters: preheating at 180 °C for 3 minutes, venting for 3 minutes, full press cycle at 180 °C for 4 minutes and cooling cycle at 20 °C for 3 minutes. A tensile test adhering to the standards of ASTM D638 was done by using the Shimadzu AGX-10kNVD machine. Figure 1 shows the overall process flow in this study.

Table 1: Formulation of the PLA/MMT nanocomposites

Sample	PLA (wt%)	Modified MMT (wt%)
PLA/0% MMT	100	0
PLA/1% MMT	99	1
PLA/3% MMT	97	3
PLA/5% MMT	95	5
PLA/7% MMT	93	7

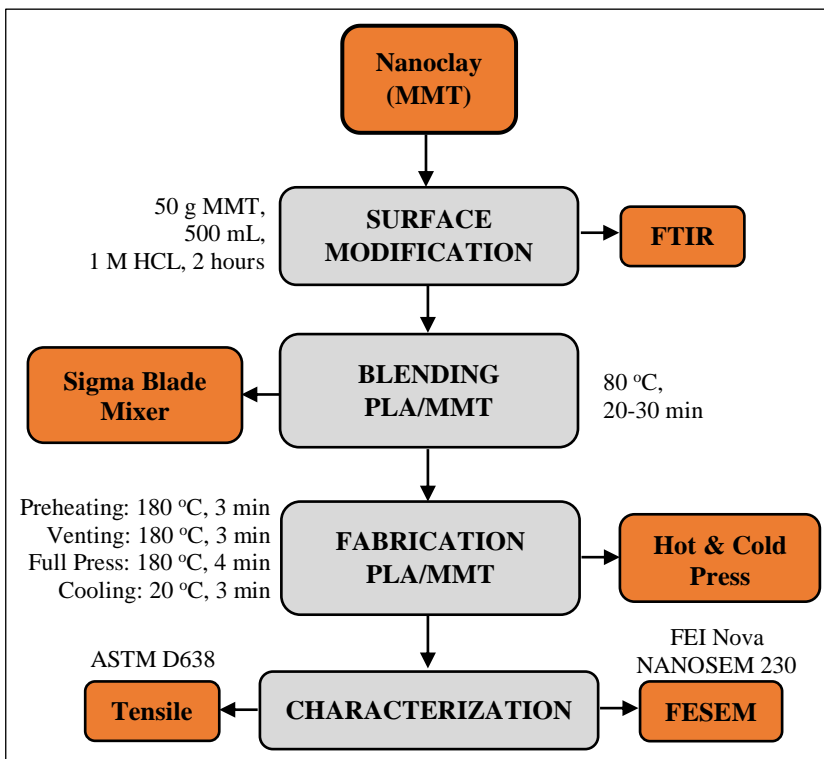


Figure 1: Overall process flow

Results and Discussion

Figure 2 shows the FTIR results of the acetylation process. Acetylation typically introduces carbonyl groups in the region around 1730 cm^{-1} - 1780 cm^{-1} . The presence of a peak associated with the C = O stretching vibration of the acetyl group on the region around 1730 cm^{-1} - 1780 cm^{-1} is shown in Figure 2. Shifts or changes in peak intensities in regions 2840 cm^{-1} - 2930 cm^{-1} led to changes in the aliphatic and aromatic regions of the FTIR spectrum. This peak result confirmed the presence of acetylation surface modification. The addition of MMT to PLA improved the interfacial adhesion between the two components and enhanced the interaction between MMT and PLA. These findings suggested that the addition of MMT to PLA has the potential to improve the composite material's mechanical properties, making it a promising material for various applications, including but not limited to disposable food packaging and cutlery in the related industry [10].

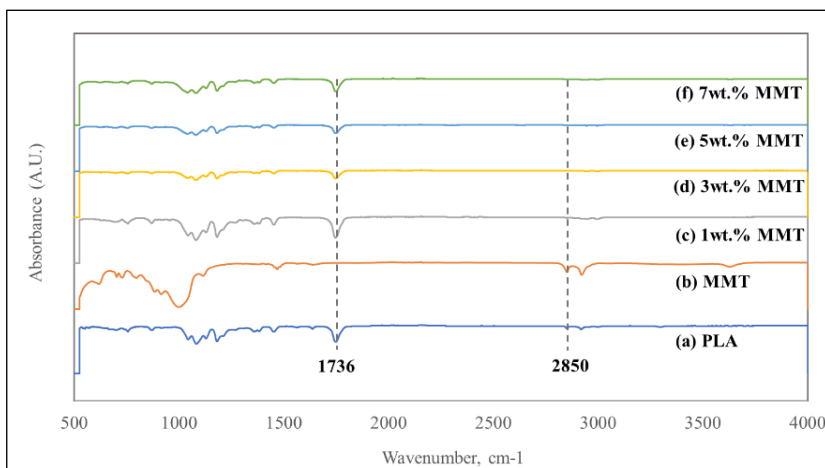


Figure 2: FTIR spectrum for; (a) PLA, (b) MMT, (c) 1 wt% MMT, (d) 3 wt% MMT, (e) 5 wt% MMT and (f) 7 wt% MMT

Figure 3 shows the tensile strength result. The addition of 1 wt% modified MMT in PLA nanocomposites increased the tensile strength up to 45% as compared to pure PLA. This is believed due to the improvement in the dispersion of nanoclay in the polymer matrix as reported by Tripathi et al. [9]. The observed relationship between enhanced toughness and reduced tensile strength and elongation suggested a trade-off in mechanical properties. Typically, when efforts are made to improve a material's toughness, there tends to be a concurrent decrease in tensile strength. This phenomenon highlights the

intricate balance and interconnected nature of mechanical characteristics in composite materials [9]-[10].

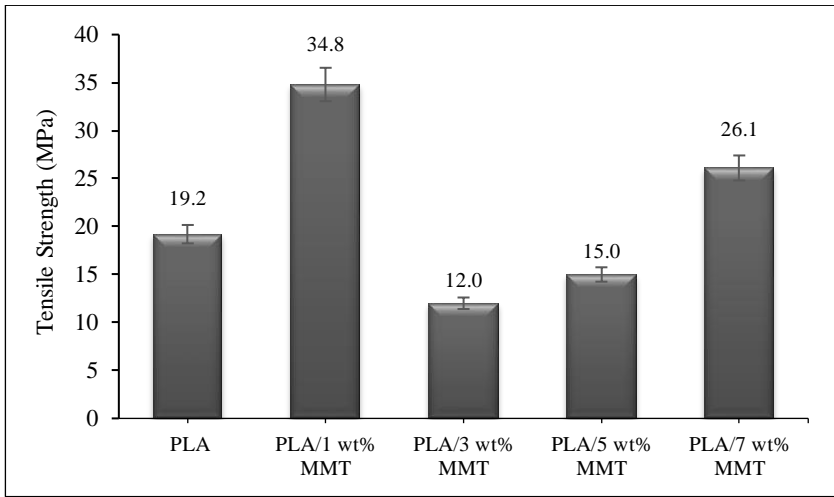


Figure 3: Tensile strength with different MMT loading contents

The results confirmed that the acetylation surface treatment of MMT improved its dispersion in the PLA matrix, resulting in a more homogeneous and potentially stronger composite. Furthermore, the presence of a high strength in a composite is indicative of a well-defined crystalline structure within the material. This correlation suggests that the composite's ability to store and release energy is linked to the arrangement and stability of its crystalline components. Understanding these interdependencies is crucial for tailoring composite materials with desired mechanical properties for specific applications [14].

The high tensile strength in sample PLA/1 wt% MMT indicated a well-defined crystalline structure within the material. The correlation between strength and crystalline structure suggests that the arrangement and stability of crystalline components play a pivotal role in determining the mechanical properties of the composite. A well-defined crystalline structure is indicative of a material's ability to endure and distribute forces effectively [15].

Elongation results in Figure 4 show the decreasing trend of nanocomposite PLA reinforced MMT. The elongation reduced to 3.2% (PLA/1 wt% MMT), 2.1% (PLA/3 wt% MMT), 2.2% (PLA/5 wt% MMT) and 2.6% (PLA/7 wt% MMT) as compared to pure PLA (3.6%). PLA/1 wt% MMT has the highest elongation at break, followed by PLA/5 wt% MMT, then PLA/7 wt% MMT, and finally the nanocomposite with PLA/3 wt% MMT has the lowest elongation at break. The addition of MMT to PLA has a negative impact

on the elongation at the break of the composite, as all the values reported for the PLA/MMT nanocomposites were lower than that of neat PLA.

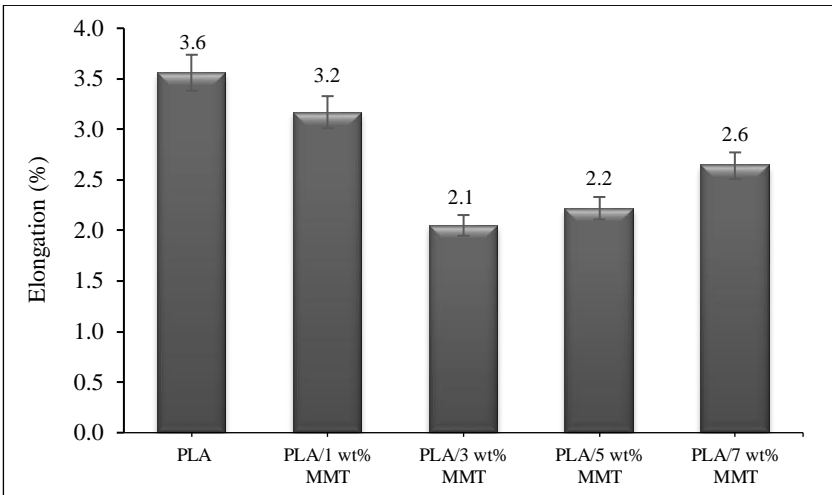


Figure 4: Elongation with different MMT loading contents

Achieving toughness in materials involves a delicate balance between strength and ductility. In this study, despite PLA inherent brittleness, improving toughness becomes a complex task. PLA is prone to brittle failure, characterised by low crack initiation energy and propagation energy. The challenge is not only in enhancing ductility, typically measured by elongation at break, but also in fortifying the material against sudden impacts, an aspect that requires targeted interventions [9].

According to Nagarajan et al. [14], modifying the material's molecular structure, incorporating additives, or exploring advanced processing techniques are advisable to address this challenge. These interventions aim to alter the fracture mechanisms, reduce the propensity and enhance the overall energy-absorbing capabilities of composites.

For maximum force, the highest value was observed for the nanocomposite with PLA/1 wt% MMT, followed by 7 wt%, 5 wt%, and 3 wt% MMT contents. This suggested that the addition of MMT can enhance the mechanical properties of PLA, with the optimal concentration being around 1 wt%. The surface modification of MMT has positively affected the mechanical properties of the PLA/MMT nanocomposites, leading to improved load transfer and increased maximum force as depicted in Figure 5.

Maximum force showed an increasing trend value as compared to pristine PLA. The highest value of 1,519.8 N was recorded by nanocomposite with PLA/1 wt% MMT content, which is approximately 86% higher than PLA

without additional MMT. The force value gradually increased to 504.4 N, 688.7 N and 1102.8 N for PLA/3 wt% MMT, PLA/5 wt% MMT, and PLA/7 wt% MMT, respectively. These values seem to indicate a poor interaction with the filler and the presence of an intercalated structure. This type of structure was expected as different studies showed that just small quantities of nanoclay, obtained the fully exfoliated nanoclay layers by melt compounding [10], [16]-[17].

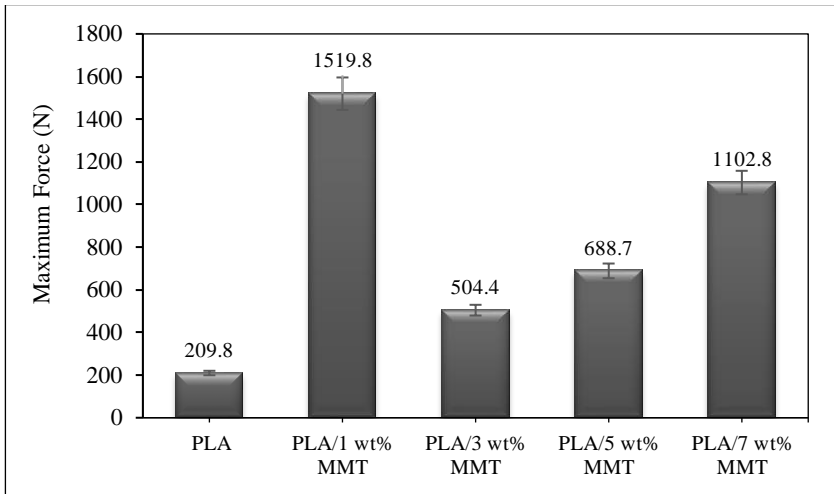
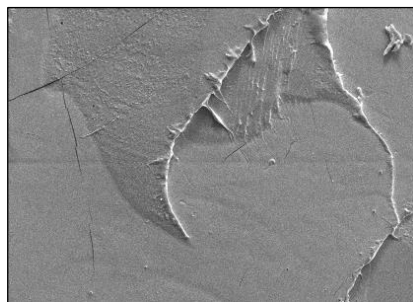


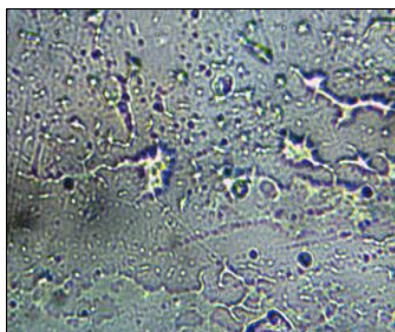
Figure 5: Maximum force with different MMT loading contents

A sudden drop in properties observed during tensile testing can be attributed to several factors, such as agglomeration of MMT during the manufacturing process of the nanocomposites and poor interfacial adhesion between the matrix (PLA) and reinforcement (MMT). The agglomerates act as stress concentration points within the material, causing weak spots under tensile loading. Whilst poor adhesion at the interface between PLA and MMT particles leads to premature failure during tensile testing. Weak interfacial bonding can result in limited stress transfer between the matrix and reinforcement, reducing the overall strength of the material [8]-[10].

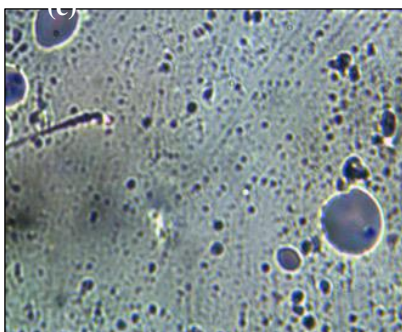
Figure 6 shows the micrographs of scanning electron microscopy (SEM) with 100x magnification views of the surface of PLA/MMT nanocomposite materials consisted of; (a) Pure PLA, (b) PLA/1 wt% MMT, (b) PLA/3 wt% MMT, (c) PLA/5 wt% MMT and (d) PLA/7 wt% MMT, respectively. The nanoclay particles were visible as small, white dots scattered throughout the micrographs.



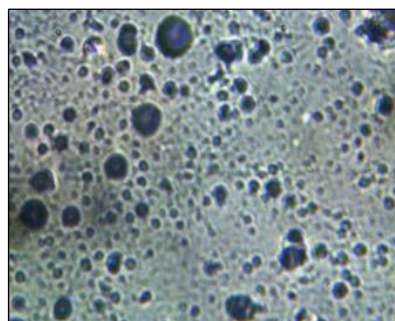
(a)



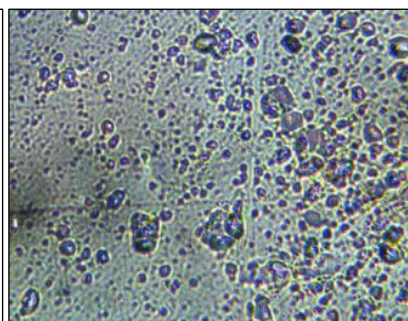
(b)



(c)



(d)



(e)

Figure 6: (a) Pure PLA, (b) PLA/1 wt% MMT, (c) PLA/3 wt% MMT, (d) PLA/5 wt% MMT, (e) PLA/7 wt% MMT (100x magnification)

The nanoclay particles appeared to be relatively well-dispersed throughout the PLA matrix in Figure 6(a). This is important because good dispersion is necessary for the nanoclay to effectively reinforce the PLA and improve its properties. The fact that the nanoclay particles were well-dispersed

suggested that the interactions were at least sufficient to prevent the particles from clumping together or debonding from the matrix [18].

Good dispersion is crucial for optimal reinforcement. It maximises the interfacial area between the nanoclay and PLA, enabling efficient stress transfer and enhancing mechanical properties. Strong interfacial interactions are vital for effective load transfer between the nanoclay and PLA. Weak bonding can lead to premature debonding under stress, negating the reinforcing effect. Voids and defects act as stress concentrators, potentially compromising the mechanical integrity of the composite [15].

There were agglomerations of MMT and voids or defects visible in Figures 6(b), 6(c) and 6(d). These aggregates and voids can reduce the strength of the composite material [19]-[20]. The number of agglomerations in these micrographs appeared to be relatively higher, so they significantly had an impact on the overall properties of the material as shown in tensile properties.

Conclusion

In conclusion, the addition of surface modified MMT to PLA/MMT nanocomposites resulted in enhanced some of the mechanical properties, including increased maximum force, Young's modulus, elongation at breaks and tensile strength. PLA/1 wt% MMT and PLA/7 wt% MMT compositions demonstrated better mechanical properties. However, in these studies, the PLA/5 wt% MMT blend was identified as the optimal composition due to its lower elongation point. The compatibility between the hydrophilic properties of MMT and the hydrophobic properties of PLA, facilitated by surface modification, synergistically improved the overall performance of the nanocomposites. Future surface modification techniques can be explored through ongoing and future research projects, expanding compatibility studies to improve the material's mechanical properties.

Contributions of Authors

The authors confirm the equal contribution in each part of this work. All authors reviewed and approved the final version of this work.

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Conflict of Interests

All authors declare that they have no conflicts of interest.

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