Novel PLA Nanocomposite Bioplastic For Use In Packaging

Grant Proposal

Raihan Ahmed

Massachusetts Academy of Math and Science at WPI

85 Prescott St, Worcester, MA 01605

Abstract (RQ) or Executive Summary (Eng)

The growing demand for plastic packaging, coupled with its environmental consequences, creates an urgent need for sustainable alternatives to conventional fossil-fuel-based plastics. Polylactic acid (PLA), a biodegradable bioplastic, is a potential replacement but suffers from significant limitations, including low thermal stability. Reinforcement with clay nanoparticles may address these deficiencies, though research to date has focused on individual nanoparticle types without exploring combinations ~~of them~~. This work seeks to advance PLA-based bioplastics by incorporating multiple clay nanoparticle types, using their distinctive properties to enhance thermal and mechanical performance. The study involves molecular dynamics (MD) simulations to ~~first~~ model ~~the behavior of~~ PLA-clay nanocomposites and identify compositions which maximize stiffness and heat resistance. The best compositions will be experimentally validated by testing mechanical, thermal, and biodegradability properti~~es,~~ to verify real-world applicability. The research will thus explain the synergistic effects of clay nanoparticle combinations within PLA. ~~Also, by~~ improving PLA's performance~~, it~~ will help advance sustainable materials for packaging, ~~thus~~ reducing environmental impact and enabling the broader adoption of bioplastics. The expected outcomes include a novel, high-performance PLA nanocomposite and an MD simulation model to guide future experiments in polymer nanocomposite design.

Keywords: polylactic acid, nanoparticles, MD simulation, bioplastics, sustainability

Novel PLA Nanocomposite Bioplastic For Use In Packaging

The demand for plastic packaging is sharply on the rise, valued at USD 384.35 billion in 2023 and growing at 3.5% every year (Grand View Research, 2023). The traditional plastics from which it is produced offer~~s~~ low costs, ~~yet~~ high availability, and ~~offer~~ the durability necessary for everyday use. However, out of the thousands of megatons of plastic produced each year, only 9% is ultimately recycled (Jambeck et al., 2017). 42% of the plastic produced is made for disposable packaging, and is considered a major source of waste globally (Rosenboom et al., 2022). This issue will persist unless quelled~~;~~ since conventional, fossil-fuel based plastics will not degrade once disposed of, and this plastic poses a danger to marine life and potentially to human health. The solution is a biodegradable alternative that retains the properties of traditional plastics, also known as a bioplastic.

Polylactic Acid

PLA, or polylactic acid, is a bioplastic that has shown promise as a potential alternative to petroleum-based plastics, especially for applications in packaging (Domenek et al., 2016). PLA's exceptional biodegradability, non-toxicity, cost, and useful mechanical properties have solidified its attractiveness as a candidate to create plastic packaging (Pereira et al., 2015). However, there are major qualms with respect to the effectiveness of PLA – namely, its low strength and its propensity to degrade rapidly at higher temperatures. ~~Luckily,~~ research has shown that reinforcing this bioplastic with nanoparticles can mitigate these issues by improving mechanical and thermal properties (Lopez et al., 2015). These nanofillers reinforce the polymer matrix, ~~and the~~ resulting composites are more

Figure 1

Effect of Clay Nanofillers

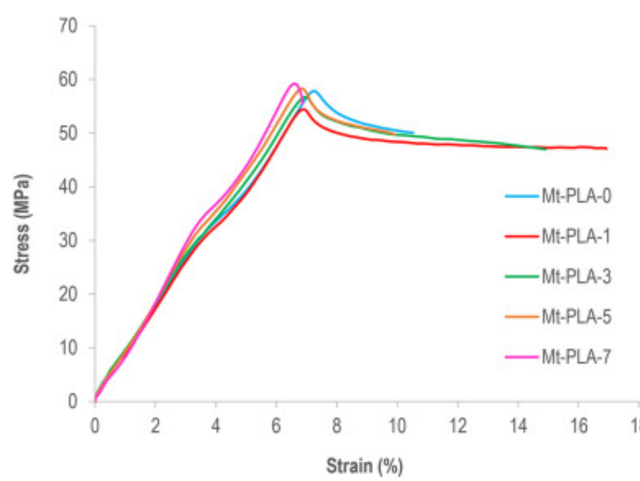

Figure 1. *Stress-strain curve for PLA-Montmorillonite nanocomposites (Gomez-Gamez et al., 2020).*

durable and thermally resilient ~~than their neat PLA counterparts~~ (Gbadeyan et al., 2022). ~~Most particularly~~, clay nanoparticles have shown promise for plastic packaging use, having excellent mechanical properties as well as improved biodegradability (Uddin et al., 2024). For example, Gomez-Gamez et al. have shown that ~~in PLA, more nanoparticles of the~~ clay montmorillonite have increased the slope of its stress-strain curve – this indicates a greater stiffness, a beneficial property for packaging (Figure 1). However, there is still ~~wide~~ room for improvement in nanofillers, namely with their thermal properties ~~even among the state of the art~~ (Lopez et al., 2015). Consequently, we intended to identify optimal nanoclay substances and their optimal compositions ~~to be added to PLA,~~ to maximize its mechanical and thermal properties.

Molecular Dynamics

One approach that has been used ~~for this type of identification~~ is ~~the simulation technique of~~ molecular dynamics (MD), which has been shown to accurately predict the properties of polymer nanocomposites (Jeon et al., 2022; Nikzad et al., 2024). For example, a study found a strong match between the glass transition temperature of a polymer calculated by MD simulations compared to experimental results, displaying a deep accuracy in predicting thermal properties of polymers (Figure 2). It involves simulating the forces involved between particles on a molecular level, integrating from a set of initial conditions. It is thus prudent to use this technique to estimate two properties of resulting plastics, both of which are predictive of their thermal and mechanical strength. The

~~**Figure 2**~~

~~*MD Simulation Effectiveness*~~

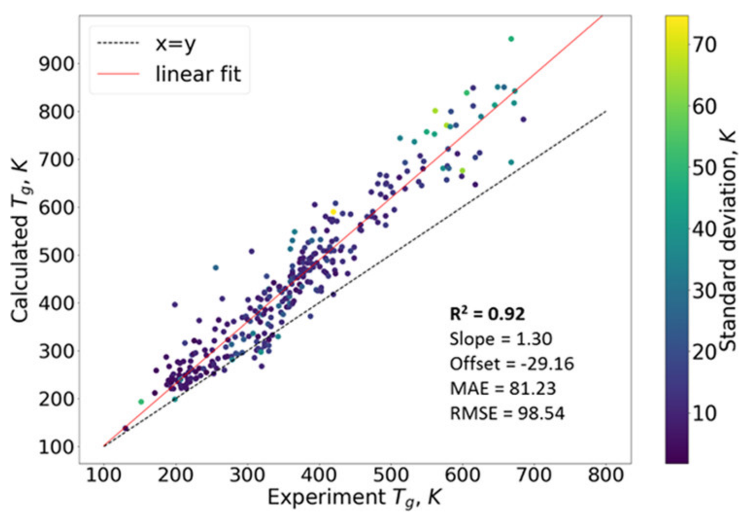

Figure 2. *Simulated versus experimental glass transition temperature for various polymers (Afzal et al., 2020).*

first is degradation as the bioplastic's temperature increases. The second is Young's modulus, which quantifies tensile stiffness.

Existing research on PLA strength has focused on applying individual nanoparticular compounds to PLA as a composite, such as silicon dioxide (Lightfoot et al., 2023), or calcium carbonate (Gbadeyan et al., 2022). However, we intend to narrow their focus to clay nanoparticles, while obtaining a wider breadth of results through the novel approach of combining multiple types of these particles, as well as exploring their optimal ratio of composition. The result of this wider range of data is the ability to narrow the field for real-world experimentation on these bioplastics. Production of PLA requires materials which may not be abundant, as well as up to 15 days of production time (Elsaeed, 2023). This heavy demand of resources motivates a solution that greatly narrows down the number of plastics undergoing physical experiments.

Experiments

After the simulations have completed, we must then prepare a plastic film for each of the leading candidates of nanoparticles and their optimal compositions. To verify the accuracy of the MD simulations, we must utilize a universal testing machine to measure the Young's Modulus and thermal properties of the resultant plastics. We must also perform a respirometry test to ascertain the biodegradability of these plastics. A statistically significant difference within the mechanical and thermal properties of the candidate bioplastic compared to neat PLA would signal the potential for more commercially viable bioplastic that could work towards a sustainable future.

Section II: Specific Aims

This proposal's objective is to outline a plan that will be used to improve PLA through the incorporation of clay nanoparticle composites that most effectively address its thermal and mechanical limitations.

Our long-term goal is to advance sustainable alternatives to petroleum-based plastics, reducing environmental impact and helping develop biodegradable packaging materials. Additionally, we hope to improve the accuracy of molecular dynamics simulations involving polymers and clay nanofiller~~s,~~ to facilitate more efficient design and optimization of polymer composites. The central hypothesis of this proposal is that combining multiple types of clay nanoparticles with PLA can improve its mechanical and thermal properties beyond that of just one type. The rationale is that many clays have distinct advantages that others lack, which may work synergistically when combined. For example, montmorillonite enhances mechanical strength in nanocomposites, while hectorite enhances thermal properties, and halloysite improves biodegradability (Uddin et al., 2024). This ability to maintain integrity at elevated temperatures is essential for improving the performance of PLA, which lacks this quality. Since PLA's widespread use in packaging and other applications has been limited by its mechanical weaknesses and sensitivity to heat, improvements in these two regards could lead to its development as a sustainable material for food packaging. The work we propose here will try to bring this about by enhancing PLA.

Specific Aim 1: Develop a molecular dynamics model that can predict mechanical and thermal properties of PLA composites with results that match real-world experimental data.

Specific Aim 2: Produce the nanocomposites that perform well in the model.

Specific Aim 3: Measure the properties of produced nanocomposites and use them to improve original model.

The expected outcome ~~of this work~~ will be a novel bioplastic ~~that is a~~ composite of PLA and multiple types of clay nanoparticles, whose properties exhibit the qualities necessary for useful and sustainable plastic packaging. A ~~MD~~ simulation model will also be produced, which can be used to predict properties of other nanocomposites in the future.

Section III: Project Goals and Methodology

Relevance/Significance

The demand for sustainable alternatives to petroleum-based plastics is partly due to increasing environmental concerns, including the impact of plastic waste on ecosystems and human health (Gbadeyan et al., 2022). Conventional plastics ~~that are~~ used for packaging, like polyethylene, contribute significantly to environmental pollution~~,~~ with limited biodegradability. On the other hand, biodegradable plastics like PLA can be a promising alternative but lack the mechanical strength and thermal stability necessary for widespread adoption. This project is significant because it aims to overcome these limitations by improving the properties of PLA by adding multiple types of clay nanoparticles. The ability to improve the mechanical and thermal properties of PLA while maintaining its biodegradability will thus reduce the environmental impact of plastic waste. This approach can help form a more sustainable future.

Innovation

In their 2024 review in advancements in nanoclay technology, Uddin et al. narrate the ways in which they have been experimented with for plastic packaging, from halloysite to montmorillonite. However, they do not state that any researchers have developed a mixture of different types of clay nanoparticles to produce a single composite (Uddin et al., 2024). Since they do mention that different types of clays have distinct beneficial properties, this ~~means our~~ research has opened up a novel path to producing more optimal polymer nanocomposites.

Lastly, we hope to innovate on the current methods of MD simulations for polymer nanocomposites. Currently, there exist significant flaws in understanding the structures of nanoclay composites, which contain layers and interactions that have not been fully explored (Uddin et al., 2024). These factors can be considered when developing a simulation that helps optimize ~~for~~ the properties that result from these interactions. Lightfoot et al. affirm that current mathematical models for predicting the properties of PLA nanocomposites are somewhat flawed, and while they match real-world results in terms of orders of magnitude, these predictions are not precise enough to be meaningful ~~(Lightfoot et al., 2023).~~ Therefore, we hope to eliminate these concerns.

Methodology

Specific Aim #1: Develop a molecular dynamics model that can predict mechanical and thermal properties of PLA composites with results that match real-world experimental data.

The methodology for this part of the project involves fulfilling three central objectives: greater sophistication in modelling chemical interactions of PLA and its nanofillers, greater accuracy relative to experimental data, and performance. Our approach involves using the MD software LAMMPS, because it is free and open source~~, as well as being~~ widely used for materials science (LAMMPS, 2024). This will produce a simulation that models the mixture of PLA and the nanoparticles, allows them to reach equilibrium, then measures properties like Young's modulus. For MD simulations, each particle must have a "force field" that dictates its interactions with other particles. This is essentially a formula for its potential energy, which can be used to predict movement of the molecules (Nikzad et al., 2024). Accurately modelling the PLA-nanoclay composites will require determining which force fields are sensible theoretically as well as producing results that match experimental data.

Justification and Feasibility. Using MD simulations to predict the properties of our polymer has a high chance of being successful. Published research has demonstrated the effectiveness of molecular dynamics simulations in predicting the behavior of polymer nanocomposites (Afzal et al., 2010; Lightfoot et al., 2023; Nikzad et al., 2024). Furthermore, as computer simulations are low-cost and low-risk, running MD simulations is highly accessible and easy to do, thus providing an alternative to cumbersome real-world experimentation.

Summary of Preliminary Data. No preliminary data has yet been gathered for this specific aim, although it is in the process of being produced.

Expected Outcomes. Nevertheless, the overall outcome of this aim is to obtain data regarding the mechanical and thermal properties of various candidate nanocomposites. This knowledge will be used to determine which combinations of clays produce nanocomposites whose properties are most optimal for plastic packaging. Those candidates will then be produced and tested in the real world.

Potential Pitfalls and Alternative Strategies. All models are imperfect, and molecular dynamics simulations are not an exception. Nikzad et al.'s MD simulations determined a Young's modulus value of 1.533 GPa for PLA, despite experiments that show it being up to 1.7 GPa (Nikzad et al., 2024). One of the issues with MD simulations of polymers is that they can only simulate a nanoscopic, small section of the polymer, which may not fully express the behavior of actual cases. This issue can be alleviated by considering other computational strategies, such as density functional theory, a quantum mechanical method used in materials science (Lightfoot et al., 2023).

Specific Aim #2: **Produce the nanocomposites that perform well in the model.**

Based on their predicted mechanical properties from the MD model, we will decide on ten nanocomposites that will be produced in real life. Producing a plastic film is simple~~,~~ yet time-consuming – as previous researchers have done, we have decided to use granular PLA purchased ~~from~~ online for these experiments. This PLA will be fully dissolved in acetone, and nanoparticles would be added if necessary. The solution would then be poured into a glass mold from which the solvent could evaporate, leaving behind a plastic film which cures for 15 days. This method is called solvent casting. Pure PLA film must also be produced as a control.

Justification and Feasibility. The previous body of scientific research is our primary justification for this strategy. Many researchers have used solvent casting to produce bioplastic films, the purpose being packaging (Zaki et al., 2023; Sudhamani et al., 2003; Gbadeyan et al., 2022).

Summary of Preliminary Data. No preliminary data has yet been gathered for this specific aim, although pure PLA is in the process of being produced.

Expected Outcomes. The outcome is expected to be ten plastic nanocomposite films, as well as one pure PLA film. These films will be used to measure the mechanical and thermal properties ~~of their respective polymers~~.

Potential Pitfalls and Alternative Strategies. Solvent casting may pose difficulties since it is challenging to distribute nanoparticle clay evenly within a polyme~~r,~~ since clay has a tendency to accumulate. This could lead to inaccuracies in mechanical and thermal tests, as properties of the polymer film will not be uniform throughout (Uddin et al., 2024). This issue can be alleviated ~~by~~ using a magnetic stirrer to ensure uniform distribution. Furthermore, PLA has a low solubility in acetone, which may impede the experiment. Chloroform is an alternative in which PLA has higher solubility (Sato et al., 2013). The long wait time, 15 days, for curing is unfortunate but unavoidable.

Specific Aim #3: **Measure the properties of produced nanocomposites and use them to improve original model.**

The PLA films will undergo a tensile test using a UTM (universal testing machine). This will allow the determination of Young's modulus. Thermal degradation can easily be quantified by raising the temperature of the polymer while measuring its mass throughout. Water permeability will be measured by placing the plastic film on a cup of water and measuring the change in mass.

Justification and Feasibility. These are standard tests which are performed in nearly all published research on the subject. (Zaki et al., 2023; Gbadeyan et al., 2022). They are also low-cost strategies that do not require much external equipment.

Summary of Preliminary Data. No preliminary data has yet been gathered for this specific aim, although it is in the process of being produced.

Expected Outcomes. The nanocomposites that the MD simulations reported to be more optimal should have a higher Young's modulus, lower propensity for thermal degradation, and decreased absorption of water than pure PLA films. The data from these analyses could be used to compare nanocomposites and determine which ones are most viable for plastic packaging.

Potential Pitfalls and Alternative Strategies. A lack of a controlled environment could significantly influence these tests negatively. A strategy to mitigate this is to ensure that water permeability tests are performed in a fume hood under constant humidity. Also, thermal tests must be performed in a room with a constant temperature. This will ensure the accuracy of the measurements.

Section III: Resources/Equipment

The first stage of the project is computational and thus does not require any external resources besides a modern computer. This computer must be equipped with the LAMMPS software, to undergo the MD simulations necessary for the experiment. Producing the plastic films will require an adequate supply of PLA pellets, as well as at least 180 ml of acetone. A fume hood will be used for creating the plastic films. For the plastic tests, a UTM is the only special equipment required, which is available at Mass Academy.

Section V: Ethical Considerations

As all experiments are either computational, or done safely under a fume hood, there are no significant ethical considerations for this project. The project introduces applications to combatting plastic pollution, which could indeed help the environment and many lives.

Section VI: Timeline

Dates	Items
08/14/24 – 11/1/24	Basic brainstorming and proposals.
11/2/24 – 12/8/24	Familiarizing with MD basics. Creating pure PLA film.
12/9/24 – 12/23/24	Obtain MD data and decide on candidate nanocomposites.
12/24/24 – 01/10/24	Create candidate nanocomposites.
1/11/24 – 1/20/24	Perform tests on nanocomposite films.

1/21/24 – 2/2/24	Analyze data.

Section VII: Appendix

This project requires little to no funding as its resources are cheap and readily available to the researchers. However, extensions to the project, such as those using equipment like thermal gravimetric analyzers to obtain data, or performing spectroscopy to determine more information about the chemical composition of the plastics, are possibilities (Gbadeyan et al., 2022). These could require funding for access to equipment. At the moment, the United States Agency for International Development (USAID), offers many grants related to eliminating plastic pollution. Thus, they provide a path for funding of future endeavors related to this project.

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