POLY (LACTIC ACID)/NANOCLAY NANOCOMPOSITES FOR PACKAGING APPLICATIONS

Maissa Akram Adi

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United Arab Emirates University

College of Engineering

Department of Chemical and Petroleum Engineering

POLY (LACTIC ACID)/NANOCLAY NANOCOMPOSITES FOR PACKAGING APPLICATIONS

Maissa Akram Adi

This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering

Under the Supervision of Dr. Muhammad Iqbal

June 2020
Declaration of Original Work

I, Maissa Akram Adi, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled “Poly (Lactic Acid)/Nanoclay Nanocomposites for Packaging Applications”, hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Dr. Muhammad Iqbal, in the College of Engineering at UAEU. This work has not previously been presented or published, or formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

Student’s Signature: _Maissa_________________________  Date: 09/July/2020
Advisory Committee

1) Advisor: Dr. Muhammad Zafar Iqbal
Title: Assistant Professor
Department of Chemical and Petroleum Engineering
College of Engineering

2) Co-advisor: Prof. Basim Abu-jdayil
Title: Professor
Department of Chemical and Petroleum Engineering
College of Engineering
Approval of the Master Thesis

This Master Thesis is approved by the following Examining Committee Members:

1) Advisor (Committee Chair): Dr. Muhammad Zafar Iqbal
   Title: Assistant Professor
   Department of Chemical and Petroleum Engineering
   College of Engineering
   Signature ____________________________ Date 10/7/2020

2) Member: Nayef Ghasem
   Title: Professor
   Department of Chemical and Petroleum Engineering
   College of Engineering
   Signature ____________________________ Date 10/7/2020

3) Member (External Examiner): Matthew Liberatore
   Title: Professor
   Department of Chemical Engineering
   Institution: University of Toledo, USA
   Signature ____________________________ Date July 10, 2020
This Master Thesis is accepted by:

Dean of the College of Engineering: Professor Sabah Alkass

Signature __________________________ Date 15/7/2020

Dean of the College of Graduate Studies: Professor Ali Al-Marzouqi

Signature __________________________ Date 15/7/2020

Copy ____ of ____
Abstract

With increasing stringent environmental regulations and attempts to reduce dependence on fossil fuels for polymer production, bio-based polymers are receiving appreciable global attention. In this context, bio-based poly (lactic acid) (PLA) is one of the most frequently used polymers in packaging application. However, despite of its high versatility, this polymer is limited in packaging applications due to its low mechanical properties. The two-dimensional nanofillers such as nanoclay and graphene are well known for improving thermo-mechanical properties of polymers at low concentrations. However, increasing higher filler concentration to improve barrier properties of polymers reduces their mechanical properties which is a drawback. This thesis investigates effects of two-dimensional nanoclays on thermal, mechanical, and barrier properties of PLA/clay nanocomposites.

The nanocomposites of PLA with clay and chemically modified clay were synthesized via solution blending method, and their thermal and mechanical properties were investigated. Several characterization techniques were used to understand chemical structure of nanoclays and thermo-physical properties of PLA/clay nanocomposites. The x-ray diffraction indicated increased dispersion and exfoliation of modified clay in PLA compared to unmodified clay. A significant decrease in percent crystallinity of PLA-modified clay nanocomposites was observed. A higher Young’s modulus and yield strength and reduced elongation at break revealed increased filler/polymer interactions in PLA/modified clay nanocomposites. Moreover, results from gas permeability revealed 75% reduction in Nitrogen gas permeability for PLA/Modified nanocomposites at 5wt%. The results could be used as fundamental understanding of clay/PLA interactions for thin film packaging applications. However, a detailed analysis of extensional rheology is required to assess feasibility of these nanocomposites for film blowing applications.

**Keywords:** PLA, Clay, Modified clay, Nanocomposites, Packaging, Dispersion.
بولي (حمض اللاكتيك)/نانوكلاي نانوكمبووز لتطبيقات التعبئة والتغليف

الملخص

مع زيادة اللوائح البيئية الصارمة ومحاولات تقليل الاعتماد على الأحافير لإنتاج البوليمر، توظف البوليمرات الحيوية باهتمام عالمي ملموس. في هذا السياق، يعد بولي (حمض اللاكتيك) الحيوي القائم على البوليمرات أحد أكثر البوليمرات استخدامًا في التعبئة والتغليف. ومع ذلك، على الرغم من تنوعها العالي، فإن هذا البوليمر محدود في تطبيقات التعبئة والتغليف بسبب خصائصه الميكانيكية المنخفضة. تُعرف حشوات النانو ثنائية الأبعاد مثل طبقة النانو والجسيمات بتحسين الخصائص الميكانيكية الحرارية للبوليمرات بتراكيب منخفضة. ومع ذلك، فإن زيادة تركيز حشو أعلى قد تحسن خصائص حاجز البوليمرات بقليل من خصائصها الميكانيكية وهو عيب. تبحث هذه الرسالة في تأثيرات الطبقات النانوية ثنائية الأبعاد على الخصائص الحرارية والميكانيكية والحاجزة للمركبات النانوية/PLA الطين.

تم تصنيع المركبات النانوية من PLA المصممة والصلصال المعدل كيميائياً عبر طريقة مزج المحلول، وتم فحص خصائصها الحرارية والميكانيكية. تم استخدام العديد من تقنيات التوصيف لفهم التركيب الكيميائي للطبقات النانوية والخصائص الحرارية الفيزيائية للمركبات PLA النانوية الطين. أشار حيود الأشعة السينية إلى زيادة تشتت وتفشل الطين المعدل في مقارنة بالطين غير المعدل. لوحظ انخفاض معنوي في النسبة المئوية لبلورة المركبات النانوية المعالجة من الطين. أظهر معامل يونغ الأعلى وقوة الخضوع والانضغاط الاستطالة عند الكسر زيادة تفاعلات الحشو / البوليمر في / مركبات نانوية معدلة من الطين. علاوة على ذلك، تم عرض نتائج تفاعلات الغازات المركبات الغذائية ونسبة 75% في نسبة غاز النترجين عند نسبة 5% من الطين المعدل. يمكن استخدام النتائج كفهم أساسي لتفاعلات الطين/PLA لتطبيقات تغليف الأغذية الراقية. ومع ذلك، هناك حاجة إلى تحليل مفصل للرياوبيولوجيا الموسعة لتقييم جدوى هذه المركبات النانوية لتطبيقات نفخ الأفلام.

مفاهيم البحث الرئيسية: حمض بولي لاكتيك، طين، طين معدل، مركبات نانوية، تعبئة وتغليف.
Acknowledgements

First of all, I would like to thank God who enabled me to complete this work. Then, I would like to express my deepest thanks and appreciation to my main supervisor Dr. Muhammad Zafar Iqbal, Department of Chemical and Petroleum Engineering (UAEU) for his guidance, support and knowledge through my two years of research work. Moreover, My extended thanks and gratitude to my co-supervisor Prof. Basim Abu-Jdayil for his continuous support and cooperation as usual.

Additionally, I would like to thank Dr. Hussein Awad, Eng. Essa Lwisa, Emmanuel Galiwango for their assistance with, XRD and TGA characterizations.

Many thanks to my beloved parents, family and friends for their encouragement and care.
Dedication

To my beloved parents and family
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### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC</td>
<td>Differential Scanning Colorimeter</td>
</tr>
<tr>
<td>$\Delta H_{cc}$</td>
<td>Cold Crystallization Enthalpy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>$\Delta H_m$</td>
<td>Melting Enthalpy</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly Lactic Acid</td>
</tr>
<tr>
<td>$T_{cc}$</td>
<td>Cold Crystallization Temperature</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting Temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo-Gravimetric Analysis</td>
</tr>
<tr>
<td>$X_c$</td>
<td>Percentage of Crystallinity</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffractometer</td>
</tr>
</tbody>
</table>
Chapter 1: Background

1.1 Overview

Bio-based poly (lactic acid) (PLA), a biodegradable polyester produced from renewable sources, [1] contains a key-position within the showcase of biopolymers for different applications such as biomedical, packaging, material strands [2].

PLA meets numerous requirements as a packaging thermoplastic and is proposed as a product gum for common packaging applications. Owing to its biodegradability, PLA can also be utilized in manufacturing bioplastics, valuables for creating loose-fill packaging, compost sacks, food packaging, and disposable flatware. In the form of fibers and non-woven materials, PLA has shown potential in upholstery, disposable garments, overhangs, feminine hygiene items, and nappies. PLA is also used as a hydrophobic block of amphiphilic block copolymers to create vesicle films of polymersomes [3]. For a few years, normal foods purveyors such as Newman’s Possess Organics and Wild Oats have been quietly utilizing a few PLA items, but the material got its greatest boost when Wal-Mart, the world’s biggest retailer, declared that they will offer a few deliver-in PLA containers.

Being an imperative aliphatic polyester and biodegradable at the same time, PLA has broad applications in biomedical engineering such as suture, bone fixation material, drug delivery microsphere, and tissue engineering [4, 5]. A major application field for microspheres is controlled drug delivery whereas a protein or peptide is homogeneously dispersed within PLA microspheres. The most commonly utilized materials for these systems are polylactide (PLA) and its copolymers with glycolide (PLGA). The adjuvant impact of biodegradable poly (D and L-lactic acid) granules is
competent of antigen release taking after intraperitoneal injection [3]. Another common application of PLA is in bio sutures. In this application a surgeon imposes a little radius of curvature but due to the even smaller suture diameter, the strains are frequently small. Similarly, small stresses and strains are normal for delicate tissue applications [6]. Table 1 provides a brief overview of several applications of PLA composites.

Table 1: Different applications of PLA/composites

<table>
<thead>
<tr>
<th>PLA/Composite</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/Polycaprolactone matrix reinforced with phosphate-based glass fibers [8]</td>
<td>Bone regenerative implants</td>
</tr>
<tr>
<td>PLA/chitosan [9]</td>
<td>Bone tissue scaffolds</td>
</tr>
<tr>
<td>PLA/gelatin nanofibers [10]</td>
<td>Tissue engineering</td>
</tr>
<tr>
<td>PLA/ketoprofen nanofibers [12]</td>
<td>Drug delivery</td>
</tr>
<tr>
<td>PLA/cork [13]</td>
<td>Fused deposition modelling</td>
</tr>
<tr>
<td>PLA/ibuprofen nanofibers [14]</td>
<td>Drug delivery</td>
</tr>
<tr>
<td>PLA/hydroxyapatite nanofibers [15]</td>
<td>Bone tissue regeneration</td>
</tr>
</tbody>
</table>

The bio-based PLA is one of the most frequently used polymers in medical packaging application. However, despite of its high versatility, these polymers are limited in widespread packaging applications due to poor mechanical properties. The two-dimensional fillers such as nanoclay are well known for improving thermal and mechanical properties of polymers at low concentrations. This will help in producing economical nanocomposites for packaging and beverage applications with low filler concentrations, and improved thermal and mechanical properties.
1.2 Relevant Literature

1.2.1 Polymers in Packaging Applications

Plastics industry overwhelmingly depends on the fossil-based polymers (~107 million tons in 2015) [16, 17] owing to their affordability and superior performance compared to naturally occurring and bio-based-polymers. The packaging industry shares a major portion (approximately 38%) of the globally produced plastics. Most frequently used polymers in packaging application are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET) [18-20]. Polyolefins such as high density PE (HDPE), low density PE (LDPE) and linear low density PE (LLDPE) dominate the packaging industry (Figure 1) [17]. The density of PE plays an important role in increasing its flexibility for various applications. For example, high strength containers (milk and detergent bottles) are produced from HDPE; flexible films and squeezable containers are manufactured from LDPE; and LLDPE is used to produce grocery bags and cling wrap films owing to its excellent flexibility and better mechanical properties [17, 21]. However, despite of their high versatility, a limiting property of polymeric materials in packaging is their inherent permeability to gases and vapors, including oxygen, carbon dioxide, and organic vapors [19, 20]. Nevertheless, several copolymers such as poly (ethylene-co-vinyl alcohol) (EVA) have excellent oxygen barrier properties required for food packaging applications. However, copolymers are typically coextruded as an internal layer or blended with other polymers.
Recently, bio-based polyolefins derived from biomass have exhibited properties identical to those of petroleum-based polyolefins [17, 22, 23]; aiming at replacing conventional fossil-based polyolefins. However, bio-polyolefins are 30% higher in cost compared to fossil-based polyolefins [17, 24], limiting their use in economical packaging applications. In general, the problems associated with biodegradable polymers are threefold: performance, processing, and cost. Although these factors are somewhat interrelated, the problems due to “performance and processing” are common to all biodegradable polymers despite of their origin [25]. In particular, brittleness, low heat distortion temperature, high gas and vapor permeability, poor resistance to prolonged processing operations have limited their applications. The application of nanotechnology to these polymers may open new possibilities for improving not only the properties but also the cost-performance efficiency [26].

Figure 1: Distribution of various polymers used for packaging industry
1.2.2 Poly (lactic acid) (PLA)

PLA is a highly versatile biodegradable aliphatic polyester derived from 100% renewable resources such as corn and sugar beets. PLA offers great promises in a wide range of commodity applications. Despite of its excellent balance of properties, the commercial viability has historically been limited by high production costs (greater than $2/lb). Until now PLA has enjoyed little success in replacing petroleum-based plastics in commodity applications, with initial uses limited to biomedical applications such as the sutures [27]. Among the biodegradable class of polymers, PLA is the most anticipated polymer for large scale packaging applications. Table 2 shows some applications of biodegradable polymers [28].

Table 2: Several biodegradable polymers with different applications

<table>
<thead>
<tr>
<th>Product</th>
<th>Composition</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polynat</td>
<td>Rye flower (80%)</td>
<td>Disposable items, flower containers</td>
</tr>
<tr>
<td>Ecofoam</td>
<td>Starch</td>
<td>Wrapping plastics</td>
</tr>
<tr>
<td>Biopol</td>
<td>PHB/PHV</td>
<td>Razors, bottles</td>
</tr>
<tr>
<td>Eco-PLA</td>
<td>PLA</td>
<td>Sanitary products, sport clothes, conditioning and packaging</td>
</tr>
<tr>
<td>Ecoflex</td>
<td>Co-polyester</td>
<td>Agricultural films</td>
</tr>
<tr>
<td>BAK 1095</td>
<td>Polyester amide</td>
<td>Disposable items, flower containers</td>
</tr>
</tbody>
</table>

1.2.3 Polymer Nanocomposites

Polymer nanocomposites are the class of materials in which nanoscale particulates such as layered clays or spherical inorganic minerals are dispersed within polymer matrices. Compared to pure polymers, polymer nanocomposites exhibit
markedly improved functional properties depending on the type and concentration of nanoparticles [29-31]. Significant scientific and technological interest has been focused on polymer nanocomposites (PNCs) over the last few decades [32, 33]. These interests are further boosted with discoveries such as carbon nanotubes, graphene, and metal-carbon complexes such as MXenes.

In general, most of the early and some of the recent efforts focused on understanding the underlying synthetic and physical chemistry [34] in conjunction with the issues of mechanical, thermal and physical properties [35] of polymer nanocomposites. Only recently more consideration has been taken to understand and exploit the physics of polymers in nanocomposites. This was persuaded by a developing acknowledgment to move beyond defining polymers with nanofillers, and towards genuinely designed, planned, and utilitarian nanocomposites. In this way, broader commercial utilization, the current fragmented understanding of the elemental angles of the structure, property and processing relationship of these materials must be addressed.

Tremendous interests in PNCs were proclaimed by the advancement of nylon-6 based clay nanocomposites developed by the Toyota research group where an uncommon set of mechanical, thermal, and physical properties were accomplished by exfoliating clay layers with a significant division of the polymer chains ionically connected by utilizing clay bound initiator during ring opening polymerization [36]. The early consideration was on the exfoliation of clay layers and its effects on property improvement; as of late, it has ended up apparently that the nature of polymer-clay interactions and high density of surface grafting changes crystalline polymorphs of
nylon-6. The altered polymorphs can be related to the changes within the mechanical and thermal properties of those nanocomposites [37].

Exceptional issues that might significantly affect the properties and handling of PNCs include changes in glass transition temperatures (Tg), as well as the crystal polymorphs and propensities [38]. Favorable interactions between polymer and nanoparticle usually result in increased Tg of the polymer. It was also found that, favorable interaction between polymer and filler results in a higher zero shear viscosity, an earlier shear-thinning transition, and a stronger shear-thinning behavior [39]. Also, the favorable polymer filler interaction restricts the mobility of the polymer chains, which results in the increase of the storage modulus and complex viscosity [40].

1.2.4 Clay Nano-Composites

Nanomaterials are the materials with nanoscopic dimensions which not only have potential technological applications in areas such as chemistry, physics, optics, materials science, biomedical sciences, mechanical devices [41], drug delivery [42], bioencapsulation but also are of fundamental interest in that the properties of a material can transition between bulk and molecular scales [41]. Generally, different nanofillers exist in numerous sizes and shapes, and can be basically classified into three categories depending on the dimensionality: Zero, one-, two-, and three-dimensional fillers. Spherical nanoparticles are considered zero-dimensional (0D), fibrous nanoparticles such as nanotubes or carbon nanofiber are one-dimensional (1D), plate-like nanoparticles are considered as 2D fillers, and nanoparticles such as graphite are considered 3D due to breadth of their structures. The plate-like nanofillers (2D) are layered materials with a thickness on the order of 1 nm, but with an aspect ratio
following their two remaining dimensions of at least 25. The most well-known 2D nanofillers are graphene and nanoclays. Graphene and clay have a thickness below 100 nm and characterized by an aspect ratio of ~100. The most common 3D nanofillers are graphite and metal oxides [43].

Among various nanoparticles, nanoclay, carbon nanotubes, and metal/ceramic nanoparticles are the most common nanofillers being studied to fabricate a variety of high-performance polymer nanocomposites [44-46]. The most important nanoparticles which are known to improve barrier performance of polymers against gases are the 2D nanomaterials such as nanoclay and graphene [47]. The plate-like morphology of the 2D nanofillers provides a tortuous path to the penetrating gas molecules, increasing their gas and vapor resistance. At the meantime, both of these nanofillers have also been reported to improve mechanical properties of the polymers. Compared to different nanoparticles, nanoclay is especially attractive as a reinforcement because it is environmentally friendly, readily available in large quantities at relatively low cost [48], and its intercalation chemistry is well studied and understood. The clay-based nanofillers are commonly alluded to aluminosilicate (also called layered silicates) based nanofillers.

Layered silicates such as montmorillonite, hectorite and saponite are widely used for preparing polymer composites to improve functional properties of polymer. The most pertinent factor in clay/polymer nanocomposites is controlling the effective dispersion of the clay by keeping up the dispersion of clay layers at nanometric scale instead of micrometric scale [49, 50]. This is attributed to high surface area of the clay platelets scattered inside polymer, offering huge surface for polymer adsorption and inter-gallery intercalation of clay [51].
Layered silicate clay nanocomposites speak to a modern lesson of crossover materials, making them interesting in academic and industrial domains due to their excellent thermal, obstruction, thermomechanical and fire-resistance properties at low nanofiller content [52]. These enhancements depend on the scattering level of layered silicates (either intercalated or exfoliated structures) inside the polymeric lattice (known as dispersion) [53]. Within the domain of polymeric nanocomposites, 2:1 layered silicates (also called 2:1 phyllosilicates) such as montmorillonite and saponite have been broadly explored as nanofillers [54]. In terms of structure, silicate layers appear as a superposition of two tetrahedrally facilitated silicon atoms on the other hand isolated by one octahedrally facilitated magnesium hydroxide moieties. Whether isomorphic substitution occur between trivalent $\text{Al}^{3+}$ particles and divalent $\text{Mg}^{2+}$ particles inside the silicate layer, structure of montmorillonite is obtained (with a layer thickness near to 1 nm) [55, 56] (Figure 2).

The electronic insufficiency display at the silicate layer (negative charges) is counteracted by $\text{Na}^+$, $\text{K}^+$, $\text{Li}^+$ and $\text{Ca}^{2+}$ particles residing inside silicate layers. The nonsufficient electrostatic forces empower joining of polar particles inside these displays as well as critical swelling capacity for the layered silicates in aqueous media. Compared to distinctive sorts of layered silicate such as vermiculites, illites, kaolinite, and smectite layered silicates exhibited superior characteristics, specifically montmorillonite. Agreeing to their most elevated swelling capacity in aqueous media, montmorillonites are heavily studied and utilized in manufacturing polymer nanocomposites [57].

It is difficult to achieve the complete exfoliation of nanosheets, but rather a mixture between intercalated and exfoliated structures is obtained. These complex
morphologies are so-called cluttered morphology or deliberate exfoliated morphology. Hence, an organic modification of layered silicates is required with, e.g. cationic trade with natural cations [53, 58] to increase effective polymer-clay interactions.

Figure 2: Structure of 2:1 layered silicate clay nanoparticles

The chemical modification helps improving dispersion of clay inside polymers. The modification is accomplished by substituting cations (Na+, K+, and Li+) on the surface of clay layers with cationic surfactants counting primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations. These surfactants alter the nature of the clay surface from hydrophilic to hydrophobic as well as expanding interlayer dividing of clay and in a similar manner, they advance more fondness and space for the polymers [59, 60]. In this respect, the inorganic cations found in the interior galleries (Na+, Ca2+, etc.) are for the most part, traded by natural ammonium, or sulfonium and/or phosphonium cations bearing at slightest one long alkyl chain, beside other substituted groups. From the literature, ammonium alkyls appear to be an
excellent organic modifying operators. These natural cations play a vital part to diminish the surface vitality between layers as well as to strengthen the fondness toward polymeric framework. Besides, use of natural cations with long alkyl chains increments, the interlayer separation is prompted in silicate layers. This allows a better diffusion of polymeric chains within silicate galleries [58].

Clay/polymer nanocomposites are a commonplace case of nanotechnology. This class of nanocomposites employ smectite type clays, such as hectorite, montmorillonite, and manufactured mica, as fillers to improve polymers properties. Smectite type clays have a layered structure. Each layer is constructed from tetrahedrally facilitated Si molecules melded into an edge shared octahedral plane of either Al(OH)₃ or Mg(OH)₂. According to the nature of the holding between these atoms, layers ought to display amazing mechanical properties parallel to the layer course [61]. Hundreds or thousands of these layers are stacked together with week van der Waals strengths to create a clay molecule. With such a setup, it is conceivable to tailor clays into various different structures in a polymer [61]. The major intrigued in utilizing clays for polymer enhancement was to break down clay particle aggregates into individual particles to create micro-sized filler reinforced polymers (Figure 3). It can be envisioned that the excellent mechanical properties of each layer in clay particles cannot work successfully in such a framework. The week interlayer bonding may act as harm initiation sites in applications. It is common to utilize high clay stacking to achieve satisfactory enhancement of the modulus, while strength and toughness of the polymer are decreased [62].

The guideline utilized in clay/polymer nanocomposites is to separate not only clay aggregates but moreover individual silicate layers in a polymer, as outlined
schematically in Figure 2. By achieving this, the great mechanical properties of the individual clay layers can work viably, whereas the number of fortifying components increase dramatically since each clay molecule contains hundreds or thousands of layers. As a result, several properties can be essentially moved forward with a low level of filler loading, usually less than 5 wt% [62].

![Diagram of Conventional Micro-Composite Approach](image1)

![Diagram of Nanocomposite Approach](image2)

**Figure 3:** Two distinct approaches applied to the production of conventional micro- and nano-composites

The primary commercial application of these materials was clay/nylon-6 nanocomposites as timing belt covers for Toyota cars, in collaboration with Ube in 1991 after which, Unitika presented nylon-6 nanocomposites for engine covers on Mitsubishi’s GDI engines [63]. In 2001, General Motors and Basell declared the application of clay/polyolefin nanocomposites as a step assistant component for GMC Safari and Chevrolet Astro vans. This was taken after by the application of these nanocomposites in the entryways of Chevrolet Impalas [64]. Recently, Noble polymers, united states, have created clay/polypropylene nanocomposites for auxiliary situate backs within the Honda Acura, whereas Ube is developing clay/nylon-12
nanocomposites for automotive fuel lines and fuel framework components. Additionally, clay/polymer nanocomposites have been utilized to make strides in obstruction resistance in refreshment applications. Alcoa CSI has connected multilayered clay/polymer nanocomposites as obstruction liner materials for enclosure applications [65]. Honeywell has made commercial clay/nylon-6 nanocomposite items for drink bundling applications [66]. More recently, Mitsubishi Gas Chemical and Nanocor have developed Nylon-MXD6 nanocomposites for multilayered polyethylene terephthalate (PET) bottle applications [67].

Mechanical properties of polymer clay nanocomposites are profoundly related to their microstructure which in turn is straightforwardly related to extent of exfoliation and dispersion of clay platelets within the polymer. The dispersion of clay platelets within melt polymer depends on thermal diffusion of polymer chains within the exhibitions and mechanical shearing activity [68]. Most likely, good exfoliation of clay platelets in a polymer matrix leads to upgraded Young’s modulus, storage modulus, and tensile strength, but significantly diminished tensile ductility and impact strength compared to neat polymer [69, 70]. For example, Compared to Nylon 6, clay/nylon 6 nanocomposites with ~4 wt% clay loading achieved 47% and 67% enhancement in tensile yield strength and Young’s modulus respectively [62]. The tensile modulus as well as the tensile strength of compatibilized polyethylene organo MMT nanocomposites at 3wt% MMT contents, were enhanced by 23% and 14% respectively in comparison with neat polyethylene [48]. Also, supercritical CO2 processed nanoclay (modified MMT) dispersed in PET increased tensile strength (10.7%) and the Young’s modulus (21.4%) compared to neat PET at only 1 wt% clay concentration. Further improvement was observed when MMT loading increased to 3 wt% [71]. The tensile strength of PLA nanocomposites with Na+ modified MMT
decreased by 25% compared with the neat PLA. The reduced tensile strength indicates poor dispersion of Na\(^+\) modified MMT in PLA. Meanwhile, the tensile strength of PLA/MMT nanocomposites films was still comparable to that of commonly used plastic films such as HDPE (22-31 MPa), PP (31-38 MPa, and PS (45-83 MPa) [72].

1.3 Thesis Objectives

The most frequently used polymers in packaging application are petroleum-based polyethylene terephthalate (PET). The objective of this thesis is to investigate the physical and the mechanical properties of bio-based poly (lactic acid) (PLA)/clay nanocomposites using 2D nanoclay fillers (MMT clay and modified clay). This thesis further helps in manufacturing economical nanocomposites for packaging and beverage applications with low filler concentrations and improved mechanical properties. Various characterization techniques such as morphological, thermal and mechanical were used to examine the effect of fillers on resultant properties.

This thesis consists of three chapters as follows: Chapter 1 contains literature review of polymers in packaging applications, PLA, and polymer nanocomposites. Chapter 2 covers literature review about PLA/clay nanocomposites. It also discusses the experimental technique used to prepare PLA/Clay nanocomposites and the characterization of nanoclay particles (clay, modified clay) as well as the characterization of PLA nanocomposites. Lastly, conclusions and future recommendations are included in Chapter 3.
Chapter 2: PLA/Clay Nanocomposites

2.1 Introduction

Approximately 99% of the plastics used nowadays are petroleum-based, and the packaging industry alone expands over 38% of these plastics. Despite of the fact that polyolefins and their subsidiaries offer great set of properties for packaging applications, they are inferred from non-renewable resources. Petroleum costs are unsteady and unpredictable worldwide, and the petroleum supply will inevitably get to be exhausted [73]. Similarly, most of these polymers have saturated (carbon-carbon) bonds in their backbones resisting biodegradation. Consequently, white contamination (emerging from the proliferation of plastic packaging materials) and landfilling issues are putting an expanding strain on the society and environment. Biodegradable polymers can provide a key turning point as renewable plastics within the course toward green packaging [17].

Biodegradable polymers incorporate common polymers (synthesized from living species such as plants, creatures and microorganisms, and extricated as polymers) and polymers synthesized from bio-based monomers industry [21, 74]. Natural polymers inferred from biomass (barring microorganisms) are plenteous and renewable in nature [75]. Natural polymers are mostly biodegradable (capable of being converted/decomposed into simple/ basic atoms by microorganisms) and hence, they reduce the strain on landfills. These polymers exist within the frame of polysaccharides (e.g. cellulose, starches and their derivatives, seaweed extricates such as carrageenan and alginites, chitosan and pectin), proteins (whey protein, gelatin, corn zein, soy protein, collagen and wheat gluten) and lipids. Cellulose is the most copious biopolymer but it is non-thermoplastic and in this way is troublesome to machine
handle [76]. Interestingly, the viscose handle depends on hazardous materials, such as carbon disulfide. In expansion, cellophanes are hydrophilic and lose their mechanical and barrier properties upon presentation to water. Subsequently, cellophanes are utilized for packaging applications as they have been generally supplanted by PP movies. Other cellulose-based polymers such as cellulose nitrates and cellulose acetic acid derivations were popular earlier to the rise of polyolefins within the 1950s [21]. These polymers were utilized for extraordinary applications especially within the packaging industry. Currently, starch and its blends are utilized in compostable bags and as free-fills in packaging disseminations as a substitution for polystyrene due to their non-adhesive characteristics.

In general, the destitute water resistance and challenges experienced within the machine processability of the key normal polymers restricted their product scale applications [77]. Critical advances have been made within the field of bio-based biodegradable nanocomposites for food packaging applications. Poly (lactic acid) (PLA)- a well-known bio-based polymer- has pulled in gigantic consideration.

PLA is commercially synthesized through the ring opening polymerization (ROP) of lactides (Figure 4) [78]. A two-step strategy for creating high molecular weight PLA (with normal molecular weight (MW) ranging from 100 to 500 kg mol\(^{-1}\)) is used. In the first step, a low MW PLA is created by polymerizing lactides in liquid state, followed by solid state polymerization to achieve high MW PLA. Naturally, lactides transcendently exist as L- and D- isomers. Consequently, the PLA synthesized via ROP consists of transcendently poly(L-lactic corrosive) (PLLA) with a few mol% of the D-lactide isomer [79].
The thermal properties of PLA such as $T_g$ and $T_m$ rely on the D-contents in PLA. For example, $T_g$ and $T_m$ of PLA with 94% L-lactide contents are 66 and 141°C, respectively. Similarly, expanding the percent composition of the D-isomer decreases crystallinity of PLA. High D-lactide content (more than 10%) renders PLA into completely an amorphous polymer. In addition, relative humidity is another factor that influences $T_g$ of PLA [80]. Due to its semi-crystalline nature, PLA has reasonably good oxygen barrier properties. For instance, PLA has 10 times better oxygen barrier characteristics than petroleum-based PP. However, PLA may have poor barrier for water vapor. PLA exhibits $1/10^{th}$ barrier compared to PP, independent of the relative humidity [81].

Moreover, mechanical properties of PLA also depend on its D- & L-contents [21]. The 100% L-lactide PLA is brittle. The presence of 2–10 mol% D-lactide isomers renders PLA for packaging applications. PLA with 94% L-lactide composition is a stiff fabric having a Young’s modulus of 2.5 GPa, which is 2 times higher than PP (1.3 GPa) and PHA (1.5 GPa). The tensile strength of PLA (74–82 MPa) is more than the
bio-based poly hydroxyalkanoates (PHAs) (15–40 MPa). In conclusion, PLA with 94% L-lactide has reasonable mechanical properties for packaging applications [82].

PLA does not viably block UV light [83] For example, up to 85% of UV-B and 95% of UV-A is transmitted by PLA films, which limits the utilize of transparent PLA for applications where UV exposure can harm a packaged product. Hence, owing to low oxygen permeability and higher UV transmission, PLA containers are not suitable for juices unless extra measures are taken to block UV light and enhance their barrier properties, and consequently hold the taste and appearance while extending item’s shelf-life. Nevertheless, PLA is transparent within the visible region, which may be an alluring highlight for the production of clear packages with effortlessly seeable items [83].

Due to the exhaustion of petroleum assets, PLA is presently showing increasing interests as an important bio-sourced polymer elective in long terms for several applications. Nevertheless, PLA endures from a few deficiencies such as low thermal resistance, heat distortion temperature and rate of crystallization. On the other hand, a few other particular properties are required by distinctive applications such as fire retardancy, antistatic to conductive electrical characteristics, anti-UV, antibacterial or barrier properties, etc.

There are numerous nanofillers (one dimensional such as nanotubes and nanofibers, two dimensional like graphene and clay and three dimensional like graphite), that have been considered, with palatable accomplishments, within the design of PLA nanocomposites [58]. The incorporation of clay nanoparticles has shown to improve performance in thermal stability, stiffness, and processability of polymers. The organically modified clays have been broadly considered. The coming
about PLA/clay nanocomposites are interesting in the packaging industry since of their prevalent mechanical, thermal, gas-barrier, and optical properties indeed at low clay content. [84].

The use of nanoclays to reinforce PLA has been reported in literature. For example, Ray et al. [85-90] demonstrated intercalation of nanoclays in PLA and resulted properties. The Young’s modulus increased by 25% with increasing clay contents whereas a noteworthy decrease in oxygen penetrability was observed. Fukushima et al. [91] synthesized nanocomposites by with 5 and 7 wt% of clays using a commercial organic modified clay (Cloisite 30B), an organically modified magnesium sodium fluoro-hectorite, and unmodified sepiolite. They observed good dispersion of clay in PLA with significant enhancements in thermal and thermo-mechanical properties of all nanocomposites. Specifically, 30B clay is a naturally altered montmorillonite (OMMT) where the natural modifier has two hydroxyl groups. The improved performance of PLA nanocomposites was attributed to the interactions between hydroxyl groups in clay and the carboxylic groups in PLA [92-94]. A number of reports have shown that the 30B clay intercalates or exfoliates well in PLA [92, 95, 96]. In addition, PLA/30 B clay frameworks were studied for degradation behavior [97], controlled drug release [98], and water vapor transmission characteristic [72].

Generally, elongation at break decreases with increasing filler contents in PNCs. However, Jollands and Gupta [99] reported increased elongation at break from 2.3 to 3.2% for the nanocomposite compared to neat PLA. Gamez Perez et al. [100] observed elongation at break rising from 4.0% for neat PLA to 5.7% and 11% for nanocomposites at 0.5 and 2.5 wt% of OMMT, respectively. Wang et al. [101] reported ductile PLA/modified MMT nanocomposites where elongation at break
increased from 5.4 to 7.9% whereas tensile modulus also progressed from 1.65 to 1.93 GPa at 1 wt% clay loading compared to neat PLA. More interestingly, elongation at break improved by 26.5 times as reported by Li et al. [102] for naturally modified rectorite (OREC) / PLA melt processed nanocomposites.

This thesis focuses on understanding how clay and modified clay nanoparticles influence the physical, thermal, crystallization and mechanical behavior of PLA/Clay and PLA/Modified clay nanocomposites.

2.2 Experimental

2.2.1 Materials

Nanoclay hydrophilic bentonite with a bulk density 600-1100 g/cm$^3$ (682659, Sigma Aldrich), Nanoclay-surface modified contains 35-45 wt% dimethyl dialkyl (C14-C18) amine with a bulk density 200-500 g/cm$^3$ (682624, Sigma Aldrich), Semi crystalline poly (lactic acid) pellets with an L-lactide:D-lactide ratio from 24:1 to 32:1 and molecular weight of 2.41X105 g/mol (PLA 4032D, Zhejiang Zhongfu Industrial Limited, Zhejiang, China) And tetrahydrofuran (anhydrous, >99.9%, Sigma Aldrich) were used as received.

2.2.2 Preparation of Nanocomposites

The PLA/Nanocomposites were prepared with different clay and modified clay concentrations (0, 1, 3, 5, 7 wt%) using solvent blending technique. Approximately, 2.5 g of PLA and appropriate amounts of clay nanoparticles were sonicated in THF solvent at room temperature for 270 minutes after which the temperature of the mixture was measured to be found as 60°C. The mixture was refluxed at 60°C under constant
magnetic stirring at 210 RPM for 2 hours. The hot mixture was dropped into deionized water resulting in coagulation of the nanocomposite suspension followed by drying under fume hood for 24 hours.

The dried samples were hot pressed using a Carver hydraulic press at 175°C for 15 minutes to produce thin sheets (~9 cm diameter, ~0.1 mm thick) followed by cooling for ~3 minutes. Finally, samples for tensile test were cut using a manual cutter (Pioneer Die-tecs) using ASTM D-638-V die into standard dumbbell-shaped specimens. A micrometer (0.001 mm resolution) was used to measure the thickness of each specimen.

2.3 Characterization tools

FT/IR-4700 Spectrometer with PRO ONE Single reflection J142A-ATR accessory (Jasco, Japan) was used to collect the Fourier transform infrared spectrum of clay, modified clay, and PLA nanocomposites over the spectral range of 400-5000 cm$^{-1}$. A thin potassium bromide (KBr) pellet was used as background.

PANalytical-XPERT-3 (Philips, Netherland) was used to obtain x-ray diffraction (XRD) spectrum using 45 kV and 40 mA working voltage and current, respectively, and Cu-Kα radiation ($\lambda = 1.542$ Å). The XRD spectra were collected within the range $10^\circ \leq 2\theta \leq 60^\circ$ for clay, modified clay, and PLA nanocomposites at 2°/min scanning speed at room temperature.

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), was outsourced at CoreLabs at King Abdullah University of Science and Technology (KAUST), KSA.
A differential scanning calorimeter (TA Instruments, 25DSC) was used to determine thermal properties such as glass transition temperature ($T_g$), cold crystallization temperature ($T_{cc}$), melting temperature ($T_m$), enthalpy of heating ($\Delta H_m$), enthalpy of cold crystallization ($\Delta H_{cc}$), and percentage crystallinity of PLA/clay nanocomposites. The experiments were performed under constant inert nitrogen flow (50 mL/min). The samples were heated from room temperature to 200°C at 10°C/min to remove thermal history followed by cooling to 20°C at 10°C/min to record $T_c$, and subsequently heated to 200°C at the same heating rate to record $T_m$. Thermal Gravimetric Analysis (TGA) was performed by using a thermogravimetric analyzer 50Q (TA Instruments, USA) in order to evaluate thermal stability of clay nanoparticles and nanocomposites. Approximately, 20 mg sample was heated up to 800°C at 20°C/min under inert nitrogen flow (50 mL/min).

Mechanical characteristics were determined by a Universal Tensile Testing Instrument (Shimadzu, AGS-X Series, 20 kN) following ASTM D638 at an extension rate of 10 mm/min at room temperature. For each sample, five specimens were tested and average were calculated and reported for tensile properties.

2.4 Results and Discussion

2.4.1 Characterization of Nano-Clay

The FTIR spectra of nano-clay and modified nano-clay are shown in Figure 5. Major peaks corresponding to Si and water were same in both spectra. The absorption peak at $\sim$978 cm$^{-1}$ was assigned to Si-OH group [103] At $\sim$1642 cm$^{-1}$, amide carbonyl group was observed. At $\sim$3613 cm$^{-1}$ stretching -OH was shown [104], while the band
at 1032 cm$^{-1}$ might be attributed to the siloxane (Si-O-Si) group stretching. The band at 913 cm$^{-1}$ was due to Al-OH [105].

For modified nano-clay Some bands appearing in more intense at 2950 cm$^{-1}$ and 2880 cm$^{-1}$ those were attributed to the C–H asymmetric and symmetric stretching of methyl group, which confirmed a successful reaction between dimethyl alkyl amine group and clay [104, 106]. Moreover, the band around 1400 cm$^{-1}$ is attributed to the presence of N–H on the structure due to amine group modification. It can be noticed that the –OH stretching which is at ~3613 cm$^{-1}$ is more intense in modified clay than clay which could be attributed to the reaction between the –OH and the water molecules which appears at ~3700 cm$^{-1}$ in modified clay [106].

![FTIR spectra of nano clay particles](image_url)
The X-ray diffraction (XRD) is an effective method to investigate exfoliation of nanoclay particles. In addition, information on dispersion of clay particles in nanocomposite films can also be obtained.

In Figure 6, the nanoclay and modified nanoclay particles show one characteristic peak at $2\theta \sim 19.7^\circ$, indicating that the d-spacing calculated using the Bragg’s law ($\lambda = 2d \sin \theta$, where $\lambda$ is the wavelength of x-rays, $\theta$ is diffraction angle, and “d” is the interlayer spacing) between the silicate layer was about 4.5 nm, corresponding to the (001) crystalline plane of clay nanoparticles [107]. Meanwhile, Figure 7 shows that, in the case of PLA/modified nanoclay, a considerable shift in d-spacing was observed, from 4.5 nm for modified nanoclay to 5.3 nm for PLA/modified nanoclay composite. This in turn, indicates that modified nanoclay particles were successfully intercalated in PLA resulting in a better exfoliation [108]. It is worth stating that, the PLA shows one intense characteristic peak at $2\theta \sim 16.6^\circ$ with a corresponding d-spacing of 5.4 nm which is almost the same as that of PLA nanocomposites. It can be noticed from Figure 7 that the most intense peak appears at $2\theta \sim 16.6^\circ$ corresponding to the reflections from (110) and (200) planes of orthorhombic $\alpha$ crystalline phase [109, 110]. The less intense peak appeared at $2\theta \sim 19.1^\circ$ corresponding to lattice plane (203) for PLA [92, 111].
The XPS analysis revealed the presence of O\(^{1s}\) core level spectra for both clay and modified clay nanoparticles. As shown in Figure 8a, for clay nanoparticles, O\(^{1s}\) is generally observed as a strong peak around 531 eV. Several studies done on clays
and micas [115] of different clay minerals showed that O$_{1s}$ is observed around 532 eV. Peak fitting revealed the presence of oxygen around 531.23 eV and hydroxyl groups appeared ~532.234 eV [116]. Almost the same peaks appeared of O$_{1s}$ core level spectra for modified clay nanoparticles as shown in Figure 8b. The slightly higher energy in O 1s spectra for modified clay may be attributed to the amine group attached onto the clay by reaction between the surface hydroxyls groups and the alkyl groups of amine.

The high resolution of C$_{1s}$ region of modified nanoclay sample showed the bands at 284.5, 286.1 and 287 eV, corresponding to C-C bond in the long chain, C-N or C-O and COOR bonds, respectively [117] as illustrated in Figure 8c. The most relevant atomic percentage variations on functionalization of bentonite with amine are the increases in carbon and nitrogen surface contents and the decrease in oxygen content, since they may confirm that amine was attached onto the clay by reaction between the surface hydroxyls groups and the alkyl groups of amine. This reaction is catalyzed by the interlayer clay water, leading to a decrease in water content (also confirmed by IR), and consequently decrease in the O% [118].

The N$_{1s}$ peak was decomposed into two components located at 402.3 and 404 eV as shown in Figure 8d. The peak at 402.3 eV maybe attributed to non-protonated nitrogen, while the peak at 404 eV can be due to the presence of protonated nitrogen [118, 119], which in turn assigned to different binding strengths (strong electrostatic and weak van der Waals links, respectively) for nitrogen from the amine group towards the clay surface [117, 120]. These results suggest a change in the atoms environment as a consequence of the grafting reaction [118].
Overall, it can be concluded from this section that the clay nanoparticles have a variety of groups, which enable them to successfully intercalated in the PLA resulting in exfoliation enhancement (illustrated by IR and XRD). In addition, interesting composition surface characteristics were shown by the XPS analysis. It was observed that the binding energy of O $1s$ of clay is slightly higher than that of modified clay due to the modification of clay with amine group which in turn is expected to play a role in enhancing the thermal as well as the mechanical properties of the PLA/Modified clay nanoparticles more than that of PLA/clay nanoparticles.

![Figure 8](image_url)

Figure 8: XPS of clay and Modified clay nanoparticles. XPS of (a) O $1s$ core level spectra of clay nanoparticles. XPS of (b) O $1s$ core level spectra of Modified clay nanoparticles. XPS of (c) C $1s$ core level spectra of Modified clay nanoparticles. XPS of (d) N $1s$ core level spectra of Modified clay nanoparticles.
Figure 8: XPS of clay and modified clay nanoparticles. XPS of (a) O 1s core level spectra of clay nanoparticles. XPS of (b) O 1s core level spectra of Modified clay nanoparticles. XPS of (c) C 1s core level spectra of Modified clay nanoparticles. XPS of (d) N 1s core level spectra of Modified clay nanoparticles (Continued)

2.4.2 Characterization of PLA nanocomposites

Figure 9 illustrates the FTIR spectra of PLA nanocomposite. The characteristic amide N–H stretching vibration (primary amine) appeared at wave number (~3500 cm⁻¹) due to hydrogen bonding. The absorption peaks at ~3010 and ~2942 cm⁻¹ were assigned to aromatic and aliphatic C–H stretching vibrations [104]. The amide carbonyl also appeared at lower wave number (~1751 cm⁻¹) due to hydrogen bonding and it also refers to esters because of the strong C=O stretching [104]. It can be noticed that, absorption peak at 1450 cm⁻¹ was given to alkane (methyl group) C-H bending. The sulfonamide appeared at ~1359 cm⁻¹ due to the strong S=O stretching. A medium appearance was noticed for C–N stretching amine at the wave length of ~1183 cm⁻¹. At ~1081 cm⁻¹ wave number, a strong C–O stretching aliphatic ether is appearing [104].
From IR analysis, it can be concluded that the main difference between the clay and the modified nanocomposites is the presence of characteristic amide N–H stretching vibration (primary amine) at wave number (~3500 cm\(^{-1}\)) for PLA/Modified clay, while this group is not existing in the PLA/Clay nanocomposites. Most likely, this can be as an attribution to the enhancement in the thermal and mechanical properties of PLA/Modified clay compared to PLA/Clay nanocomposites.

![FTIR spectrum of PLA/Modified clay nanocomposites](image)

Figure 9: FTIR spectrum of PLA/Modified clay nanocomposites

In order to study the influence of nanoclay and modified nano clay on crystallinity (\(X_c\)), melting (\(T_m\)), cold crystallization (\(T_{cc}\)) and glass transition (\(T_g\)) temperatures of PLA/Clay and PLA/modified nanocomposites, a differential scanning calorimeter (DSC) was used. For the purpose of removing the thermal history, samples were heated rapidly above their melting temperatures. The second heating cycle was used to record \(T_m\) and \(T_g\) as discussed in the following section. Figure 9 illustrates \(T_m\) and \(T_g\) values for pure PLA, PLA/clay and PLA/modified clay nanocomposites at 7
wt%. It can be noticed that, both clay and modified clay enhanced the glass transition of PLA. However, this enhancement is slightly more noticeable for modified clay where T_g rised up from ~52°C for PLA to ~54°C for PLA/modified clay composite, attributed to increased polymer-filler interactions.

The nanocomposites PLA/Clay exhibited T_{cc} peak values (~105°C) which is almost similar to that of PLA. However, PLA/Modified composites clay showed an increase in the T_{cc} (~112°C) compared to that of PLA. The enhancement in the T_{cc} of the PLA/Modified clay nanocomposites indicate nucleation behavior of modified clay nanofiller. Compared to PLA T_m value (~165°C), PLA/Modified clay nanocomposites T_m slightly increased (~167°C), while, a slightly lower T_m value was recorded for PLA/Clay nanocomposites (~161°C).

In conclusion, the glass transition temperature as well as cold crystallization was enhanced by modified nanoclay incorporation with PLA, whereas the melting behavior did not change significantly. It is worth stating that, the produced PLA/Modified nanocomposites show promising thermal characteristics compared to several PLA composites. For instance, the maximum observed T_m (169°C) of PLA/Clay at 5wt% and the maximum observed ΔH_m (42 J/g) of PLA/Modified nanocomposites at 5wt% are higher than reported values of PLA/cellulose crystal composites for which the T_m and the ΔH_m are 148°C and 22 J/g, respectively. While they have higher Xc (24%) than that of PLA/ clay and modified clay nanocomposites at 5wt% filler [121]. Also, it was found that, the PLA/graphene oxide nanosheets composites have lower values of T_m (161°C), ΔH_m (36 J/g), T_{cc} (109°C) and Xc (1.9%) compared to the produced PLA/clay and modified clay at 5wt% [122]. Moreover, the maximum T_g value of PLA/clay and modified clay nanocomposites (57°C) is higher
in comparison with PLA/microcrystalline cellulose (56°C) at 1 wt% filler. For the same
PLA/microcrystalline cellulose, the Tm and ΔHm values of 149°C and 24 J/g, respectively, are also lower than that of the resulted PLA/clay and modified clay
nanocomposites at 5 wt% [123].

Figure 10: DSC curves of PLA, PLA/Clay and PLA/Modified Clay nanocomposites
at 7 wt% clay loadings

Table 3 summarizes the DSC data of PLA, PLA/Clay and PLA/Modified clay
nanocomposites. The highest values of the melting temperature (Tm), glass transition
temperature (Tg) and cold crystallization temperature (Tcc) were recorded for
PLA/Modified clay nanocomposites. On the other hand, it can be shown that the
enthalpy of cold crystallization (ΔHcc) increased for both PLA/Clay and
PLA/Modified clay nanocomposites compared to that of PLA with increasing clay
contents, whereas enthalpy of heating (ΔHm) and percentage crystallinity (Xc) of
PLA/Clay nanocomposites and PLA/Modified nanocomposites decreased under the
same conditions. However, modified clay reduced crystallinity of PLA more than what was observed in PLA/clay nanocomposites. Thus, a higher elongation at break and lower tensile modulus are expected for PLA/modified clay nanocomposites.

The percentage crystallinity ($X_c$) of PLA, PLA/Clay and PLA/Modified nanocomposites was calculated using the following equation [124]:

$$X_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H^\circ_{100\%} (1 - \theta)} \times 100\%$$

[1]

Where $\Delta H_m$ is the experimental enthalpy of melting obtained from the DSC melting endotherms, $\Delta H^\circ$ is the enthalpy of melting of the 100% crystalline PLA (93.7 J/g) [125], $\Delta H_{cc}$ is the enthalpy of cold crystallization, and $\theta$ is the weight fraction of the filler in the matrix. The $X_c$ decreased with increasing filler content in both nanocomposites compared to PLA ($X_c\% = 42.8$) (Figure 10). The PLA/Modified clay nanocomposites exhibited more decrease in crystallinity even at higher clay contents which might be beneficial for manufacturing transparent PLA/Modified clay nanocomposite thin films.
Table 3: DSC data of PLA, PLA/Clay and PLA/Modified clay nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Filler Wt%</th>
<th>T\textsubscript{g} (°C)</th>
<th>ΔH\textsubscript{cc} (J/g)</th>
<th>T\textsubscript{m} (°C)</th>
<th>ΔH\textsubscript{m} (J/g)</th>
<th>X\textsubscript{c} %</th>
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</thead>
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<td>PLA</td>
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<td>52±1.2</td>
<td>10.4</td>
<td>165±1.03</td>
<td>50.5</td>
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</tr>
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<td>168.6</td>
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<td>56±1.4</td>
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<td>169±1.05</td>
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<td>55.7</td>
<td>30.5</td>
<td>168.6</td>
<td>38.4</td>
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Figure 11: The effect of PLA/Clay and PLA/Modified clay nanocomposites on crystallinity
Thermogravimetric analysis (TGA) was used to investigate thermal stability of PLA and PLA nanocomposites. Figure 11 shows the weight loss curves as well as the corresponding derivative weight loss of pure PLA and PLA nanocomposites. The thermal stability of PLA/Clay nanocomposite was lower than that of PLA whereas PLA/Modified clay exhibited higher thermal stability compared to PLA. The thermal decomposition temperature (T_d) of PLA/Clay nanocomposite is lower than that of PLA. On the other hand, T_d of PLA showed an enhancement by ~7°C towards higher temperature, from ~380°C to ~387°C for PLA/Modified clay nanocomposite.

The TGA results are presented in Table 3 quantitatively. For PLA/Clay nanocomposite, 5% weight loss occurred at ~311°C while PLA/Modified clay nanocomposites lost the same weight percent at ~344°C. This means that the thermal degradation of PLA/Modified clay nanocomposite occurs at higher temperature compared to PLA which lost 5% of its weight at 336°C. Moreover, it could be stated from Table 4 that the overall weight loss (%) of PLA nanocomposites enhanced from 99% overall weight loss for PLA to 93.5% and 94.5% weight loss for PLA/Clay and PLA/Modified nanocomposites respectively. The results indicate improved interactions between PLA and modified clay that consequently, might have increased thermal stability of the nanocomposites.
The influence of PLA/Clay and PLA/Modified clay nanocomposites on mechanical properties was investigated using a universal testing machine. Tensile stress-strain curves and the fracture points ($\varepsilon_f$, $\sigma_f$) (represented by arrows) of pure PLA, PLA/clay, and PLA/Modified clay matrices are shown in Figure 13. Compare with PLA/clay and PLA/Modified clay, PLA is observed to experience more ductility prior to failure that took place at 20 MPa and 10.24% elongation. This necking/strain
hardening could occur mainly due to the sudden deformation and then the stretching as stress increases [126] and it can be due to dislocation movements and dislocation generation within the crystal structure of the material [127]. On the other hand, embrittlement behavior was observed for PLA nanocomposites system due to the incorporation of clay and modified clay to the PLA matrix which eliminates the orientation apparent strain hardening experienced by the pure polymer [128]. The break stress of PLA/clay, and PLA/Modified clay is higher compared to pure PLA for the same strain, indicating that the addition of clay and modified clay improved effectively the modulus and strength of PLA matrix. It is worth stating that, the fracture stress value of the prepared PLA/Modified clay composite (~30 MPa) is higher than that of PLA/ microcrystalline cellulose (MCC) and silver (Ag) films (~ 21 MPa) [123]. While it is lower than that of PLA/cellulose nanofiber films [129] and PLA/graphene nanoplatelet [128] with ~ 58 MPa and ~59 MPa, respectively.

![Stress-strain curves of PLA, PLA/Clay, and PLA/Modified clay composites](image)

Figure 13: Stress-strain curves of PLA, PLA/Clay, and PLA/Modified clay composites
The effects of clay and modified clay on the Young’s modulus and yield strength of the PLA/nanocomposites are shown in Figures 14 and 15 respectively. The PLA/clay and PLA/modified clay exhibited Young’s moduli of \(~697\) MPa and \(~764\) MPa at \(7\) wt\% respectively, which were higher than neat PLA \((~502\) MPa). In general, the PLA/modified clay nanocomposites showed lower modulus value than that of PLA/Clay nanocomposites which might be attributed to low crystallinity observed in DSC analysis for PLA/modified clay nanocomposites. However, PLA/clay nanocomposites have lower of tensile yield strength than PLA/Modified clay on each % increase. The modified clay had a noticeable beneficial effect on the tensile yield strength of the nanocomposites which increased with increasing modified clay content (1 and 3 wt\%). A dramatic increase in the yield strength from \(~12\) MPa for PLA up to 16 MPa for PLA/Modified clay composite by 3 wt\% modified clay content, indicating 33% enhancement in the yield strength. This improvement can be due to the well dispersed of modified clay particles in the polymer matrix in comparison with nanoclay particles. The reported values of PLA/graphene nanoplatelets [128], PLA/cellulose nanocrystals [121] and PLA/fiber [130] are 1290 MPa, 1442MPa and 8300 MPa, respectively. Several studies reported the yield strength value of different types of PLA composites. For instance, the yield strength of PLA/nanofiber [131] PLA/cork [13] and PLA/starch [132] are 50.7 MPa, 38.3 MPa and 28 MPa respectively, which illustrate that clay is similar to cork and starch in improvement but orders of magnitude less than graphene and cellulose nanomaterials.
Figure 14: Young’s modulus (MPa) of PLA nanocomposites

Figure 15: Yield strength (MPa) of PLA nanocomposites
Usually, a well-developed polymer/clay nanocomposite results in highly increased mechanical strength compared to the pure polymer matrix since uniform dispersion of the nano sized clay particles produces an ultra-high interfacial area and ionic bonds between the nanoclay and the host polymer [133-135]. In the present study, the addition of modified nanoclay enhanced both the tensile yield strength compared to nanoclay. This indicates that the modified clay particles are well dispersed in the polymer matrix in comparison with nanoclay particles [136] due to the reaction occurring between the hydroxyl group and amine group of modified clay and the carboxyl groups of PLA. Also, the increased degree of modified clay dispersion found through narrow-angle X-ray scattering measurements promotes the formation of a larger interfacial area and subsequent interfacial interaction between modified clay and PLA. Therefore, the stress transfer from the polymeric matrix to the inorganic phase increases, leading to enhance the tensile strength and modulus of the PLA composites [72].

Table 5 and Figure 16 show the elongation at break values of PLA/Clay and PLA/Modified clay nanocomposites. Generally, the elongation values decreased with increasing clay content in both PLA/Clay and PLA/Modified clay nanocomposites. The elongation reduction of PLA/Modified clay composites is lower than that of PLA/Modified clay composites. These results propose that PLA/Modified clay nanocomposites exhibited higher toughness and ductility compared to PLA/Clay nanocomposites, which showed a brittle behavior. A similar behavior was observed by Guohua et al (2006) for PVA/methylated-cornstarch composites [137]. Though the elongation at break decreased after compounding with nanoclay, those of the composite films are still comparable and competitive to those of widely used plastic films such as PVA/methylated-cornstarch, and starch films, of which the elongation at
break values are in the range of 1.53-1.64 and 0.94-2.47, respectively [137, 138].
Moreover, the reported elongation at break values of PLA/Clay and PLA/Modified clay at 3 wt% are 5.88 and 8.36 respectively, which were found to be greater than that of cellulose nanocrystals (5.5%) for the same % filler content [121].

Table 5: Elongation at break of PLA, PLA/Clay and PLA/Modified clay nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Filler (wt%)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>PLA/Clay</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6</td>
</tr>
<tr>
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<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>5.2</td>
</tr>
<tr>
<td>PLA/Modified clay</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8</td>
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<td>6</td>
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<td></td>
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</tbody>
</table>

Figure 16: Elongation at break for PLA composites
Among the nanoclays tested, modified nanoclay was more effective in maintaining tensile yield strength property than the nanoclay, indicating that the modified nanoclay is more compatible and has better homogeneous dispersion with PLA, as compared to the nanoclay. However, high modified nanoclay content could led the particles of the modified nanoclay to agglomerate within the matrix, causing a poor dispersion and thus less enhancement in mechanical properties. For mechanical properties enhancement such as modulus and tensile yield strength, the optimum modified clay content is 7 wt% and 3 wt%, respectively.

For the nitrogen gas permeability test, the samples were cut into circular shape with diameter of 0.037 m and 0.0001 m thickness. Then the sample was placed between the two plates which are made of stainless steel. The Nitrogen gas permeability of each sample was measured under a pressure ranged between 0.5 and 4 bar.

The apparent permeability ($k_a$), in m$^2$, was calculated at constant pressure using the Hagen-Poiseuille expression for a compressible fluid. Since gases are compressible, the inlet pressure $P$ (applied test pressure (absolute)) at which the flow rate ($Q$) is measured must be taken into account in addition to the outlet pressure $P_{atm}$ (atmospheric pressure). The following equation was used to calculate the apparent permeability ($k_a$) [139]:

$$k_a = \frac{(2.Q.P_{atm}.L.\mu)}{(P_i^2 - P_{atm}^2)A}$$

[2]
Where,

\[ A = \text{cross-sectional Area (m}^2) \]

\[ L = \text{sample thickness crossed by the flow (m)} \]

\[ \mu = \text{gas dynamic viscosity (Ns/m}^2) \]. For nitrogen, \( \mu = 1.76 \times 10^{-5} \text{Ns/m}^2 \) at 20°C [140]

\[ P_i = \text{inlet pressure (Pa)} \]

\[ Q = \text{measured gas flowrate (m}^3/\text{s}) \]

Generally, it can be noticed that as the pressure increases the permeability of neat PLA as well as of the nanocomposites films decrease as shown in Figure 17 and 18. From Figure 17, it can be noticed that, for PLA/Clay nanocomposites, there is almost no noticeable enhancement in the permeability except for 7 wt% of clay content with 60% reduction in nitrogen permeability at 400000 Pa. This improvement in barrier property is because of the tortuous path being created by the clay particles which retards the diffusion of the gas molecules through the matrix region. As clays are crystalline materials, they are expected to increase the barrier properties by creating a maze or “tortuous path” that restricts the progress of the gas molecules to pass through the polymer matrices [141]. In comparison, almost all the PLA/Modified nanocomposite films showed better nitrogen barrier properties than neat PLA films as shown in Figure 18. Amongst all the PLA/Modified nanocomposites, the nanocomposite having 5 wt% of modified clay content exhibited the highest reduction in nitrogen permeability, approximately 76% which is higher than that (26%) of PLA/Clay the same filler content. The enhanced nitrogen reduction of PLA/Modified clay nanocomposites compared to that of PLA/Clay nanocomposites is attributed to the improved dispersion and exfoliation of PLA/Modified clay in comparison to that
of PLA/Clay nanocomposites [142] as was supported by the XRD analysis. This is due to the dispersion of amine of the modified clay in the PLA matrix which resulted in the effective hydrogen bonding interaction among amine group and carbonyl back bone of PLA which in turn improved the tortuosity passage for nitrogen gas [109].

![Graph](image-url)

Figure 17: Nitrogen gas permeability of PLA/Clay nanocomposites
Figure 18: Nitrogen gas permeability of PLA/Modified clay nanocomposites
Chapter 3: Conclusions and Future Recommendation

3.1 Conclusions

In conclusion, in this study, clay and modified clay nanoparticles were incorporated with PLA to produce PLA/clay and PLA/modified clay nanocomposites using solvent blending technique. PLA chains intercalate galleries of clay nanoparticles. The thermal, mechanical, and morphological properties of the produced nanocomposites were characterized. The effect of modified clay on the exfoliation and dispersion improvement of the PLA/modified clay nanocomposites was confirmed by the appearance of wider peak than that of the PLA/clay nanocomposites in the XRD for which the peak also shifted to lower 2θ. Generally, the highest values of the melting temperature (T_m), glass transition temperature (T_g) and cold crystallization temperature (T_cc) were recorded for PLA/Modified clay nanocomposites. On the other hand, it can be shown that the enthalpy of cold crystallization (ΔH_cc) increased for both PLA/Clay and PLA/Modified clay nanocomposites compared to that of PLA, whereas, the enthalpy of heating (ΔH_m) and percentage crystallinity (X_c) of PLA/Clay nanocomposites and PLA/Modified nanocomposites decreased in comparison with PLA. Due to the chemical structure and low crystallinity of modified nanoclay, its addition reduced crystallinity of PLA more than the addition of nanoclay which is beneficial for manufacturing transparent nanocomposite thin films. Therefore, higher elongation at break and lower tensile modulus were shown by PLA/Modified clay nanocomposites, thus, higher toughness and ductility. In addition, analysis of mechanical data indicates that the optimum modified clay concentration in the PLA/Modified clay nanocomposites might be 3 wt%. Higher than 3 wt% modified clay might cause destitute dispersion of modified clay nanoparticles due to
agglomeration coming about in diminished mechanical properties. Moreover, the results of nitrogen gas permeability revealed that, the PLA/Modified clay nanocomposites exhibited the best nitrogen gas permeability reduction at 5 wt%, which is higher than that achieved by PLA/Clay nanocomposites at the same filler load.

3.2 Future Recommendations

Further work may include extensional rheology to assess feasibility of these nanocomposites for film blowing applications. Moreover, melt blending technique could be used for the preparation of the same type of PLA nanocomposites prepared in this study in order to investigate the differences. This would be accommodating in investigating the impact of method utilized to prepare such samples on the properties of the delivered PLA nanocomposites.
References


