DEVELOPMENT OF BIODEGRADABLE -POLYLACTIC ACID - DATE PALM WASTE COMPOSITE AS THERMAL INSULATION MATERIAL

Mohamed Saeed Barkhad

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DEVELOPMENT OF BIODEGRADABLE -POLYLACTIC ACID - DATE PALM WASTE COMPOSITE AS THERMAL INSULATION MATERIAL

Mohamed Saeed Barkhad

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

Under the Supervision of Professor Basim Abu-Jdayil

April 2019
Declaration of Original Work

I, Mohamed Saeed Barkhad, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled “Development of Biodegradable Polylactic Acid – Date Palm Waste Composites as Thermal Insulation Material”, hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Professor Basim Abu-Jdayil, 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 Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions.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.

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Abstract

This study aims to develop a green polymer composite from local natural waste, such as date pit powder (DPP) and date palm wood powder (DPWP), as an insulating material. The recycle and reuse of natural waste as filler for green insulation materials has many significant benefits for the environment of the UAE.

Date palm waste was mixed with a poly lactic acid (PLA) polymer with various proportions in a melt extruder. The mixtures produced were then shaped differently after testing in a thermal compression machine. These composites were tested to evaluate their physical (water absorption, chemical resistance and bulk density), thermal (thermal conductivity, thermal diffusivity, and degree of crystallization) and mechanical properties.

As thermal insulation material should exhibit low thermal conductivity and acceptable levels of mechanical strength, the samples of pure PLA were subjected to different annealing conditions after the thermal compression stage. The PLA specimens were heat treated at 95°C at different time intervals before cooling. The 24-PLA samples subjected to longer annealing times have higher strength, greater thermal conductivity and improved density. Based on these results, processing parameters for composite production (melting and mixing temperatures and annealing conditions) were optimized in order to produce composites with optimum thermal conductivity and mechanical strength.

The results showed that, date palm wood powder (DPWP) and date pit powder (DPP) were alternative fillers when combined with PLA to produce a stable green thermal insulation material. The use of date palm wood powder (DPWP) in different ratios, ranging from 0 to 50 wt.%, produced composites with a thermal conductivity value between 0.0692 and 0.0757 $W/(m.K)$, while the minimum thermal conductivity was reported at 30 wt.% DPWP content. On the other hand, the composites containing 0 - 40 wt. % DPP had a thermal conductivity in the range of 0.0712 to 0.0794 $W/(m.K)$. The lowest thermal conductivity was found in composites with a DPP content of 40 wt. %. In addition, the thermal diffusivity of both types of composite decreased as filler content increased, reaching a minimum value of 0.043 and 0.036 $mm^2/s$ for the PLA-DPWP and PLA-DPP composites, respectively.
The PLA-DPP composites showed higher water retention than the PLA-DPWP composites. The water retention has found to increase as filler content increased. At 50 wt. % of DPWP, water retention was less than 1.5%, while in the case of 40 wt.% DPP composites, water retention reached approximately 6%.

For both types of composite, adding fillers to the PLA matrix initially reduced compression strength until it reached a constant value (~ 65 MPa) at 30% filler content. Replacing 50 wt. % of pure PLA with DPWP decreased the compression strength by 32%, while it increased the compression modulus by 11%. On the other hand, 40 wt.% DPP filler reduced compression strength and modulus by 33% and 17.5%, respectively. Furthermore, scanning electron microscopy (SEM) was used to investigate the microstructure of the composites and to explain their thermal and mechanical behavior.

Ultimately, although addition of both types of waste to the PLA matrix reduced mechanical strength, the composites displayed good mechanical properties when compared with many commercial thermal insulators and construction materials currently available. Moreover, replacing part of the concrete used in a typical building wall with PLA-DPWP or PLA-DPP composites increased the R-value by 220.2 % and 211.8 %, respectively. Therefore, recycling of cheap natural waste as filler materials for green thermal insulators is a potentially significant benefit to both the economy and environment.

**Keywords**: Green thermal insulators, composite, poly lactic acid, natural waste, date wood powder, date pit powder.
تطوير عوازل حرارية معتمدة على البوليمر القابل للتحلل مع مخلفات التخيل

المشروع

يهدف هذا البحث لتطوير عوازل معتمدة على الخليط الناتج من البوليمر القابل للتحلل والمخلفات المحلية الطبيعية من النخيل مثل خشب النخيل المطحون وبذور التمر المطحون. تدوير هذه المواد واستخدامها كمواد ملائمة له تأثير كبير على طبيعة دولة الإمارات العربية المتحدة.

استخدم البولي اثيل أكسيدي (PLA) كمادة البذرة، وخلط مع نسب مختلفة من المخلفات الطبيعية باستخدام البثق (Extruder). ومن ثم تم تعرض الخليط الناتج إلى الضغط والحرارة باستخدام آلة الضغط والحرارة (Hot-press) لإنتاج العينات المطلوبة. لقد تم فحص هذه العينات من ناحية الخواص الفيزيائية (امتصاص الماء، مقاومة الكيميائية، الكثافة الحرارية (قابلية توصيل الحرارة وتحمل الحرارة) والخواص الميكانيكية (قوة الضغط، معامل الضغط).

تبتسم المواد العازلة بانخفاض توصيلها للحرارة. فلذلك تم دراسة البولي اثيل أكسيدي (PLA) تحت ظروف مختلفة للتلدين. حيث تعرضت للتلدين عند درجة مئوية 95 درجة مئوية لمدة 24 ساعة. أظهرت توصيلة للحرارة أعلى، قوة ضغط أعلى وكثافة أعلى. من هذا الدراسة تم استخلاص بعض العوامل والشروط لتشكيل وتحضير المركبات تتميز بخصائص ميكانيكية وتوصلية حرارية مثالية.

أظهرت النتائج أن خشب النخيل المطحون وبذور التمر المطحون يمكن استخدامهما كمواد ملائمة في العوازل الحرارية الخضراء. إضافة خشب النخيل المطحون بنسبة تتراوح بين 0-50% من الوزن له تأثير على قابلية التوصيل الحراري حيث كانت أقل قيمة لها (0.0693 W/(m.K)) عند 50% من الوزن. وفي الجانب الآخر، إضافة بذور التمر المطحون بنسبة تتراوح بين 0-40% من الوزن له تأثير على قابلية التوصيل الحراري حيث كان أقل قيمة لها تساوي (0.07125 W/(m.K)) عند 40% من الوزن. بالإضافة إلى ذلك، معامل إنشار الحراري انخفض مع زيادة المادة المثالية، حيث
وصلت لـ $(0.043 \ m^2/s)$ لعينات PLA-DPP بينما لعينات PLA-DPWP انخفضت لـ $(0.036 \ m^2/s)\) و من منظور الخواص الميكانيكية، و مقارنةً مع بولي لاكتيك النقي، فإن تبديل 50% من وزن بولي لاكتيك بخشب النخل المطحون، أدى إلى انخفاض قوة الضغط بنسبة 32% بينما تزايد معامل الضغط بنسبة 11%. بالإضافة إلى ذلك، بذور التمر المطحون أدى لخفض قوة الضغط ومعامل الضغط بنسبة 33% و 17.5% على التوالي. المسح المجهري الإلكتروني (SEM) قد استخدم للتحقق من البنية المجهرية للمركبات المحضرية. بالإضافة إلى ذلك، المركبات PLA-DPWP قد اظهرت قيم ممتازة في تجربة امتصاص الماء ولكن كان قيم امتصاص الماء لعينات PLA-DPP أعلى من قيم امتصاص الماء لعينات DPWP وأخيرًا، على الرغم من أن إضافة المواد المائنة إلى بولي لاكتيك اسيد يؤدي لخفض الخواص الميكانيكية ولكنها تظهر قيم أعلى من تلك الخواص الميكانيكية ل كثير من المواد العازلة المتاحة تجارياً. علاوةً على ذلك، فإن تبديل جزء من سمك الخراسان التي تكون جدران المباني بالمركبات المحضرية تساهم على زيادة مقاومة الجدار لتوصيل الحرارة بنسبة 220.2% إذا كانت المادة المائنة خشب النخل المطحون و211.8% إذا كانت المادة المائنة بذور التمر المطحون. ونتيجة لذلك، فإن استخدام مثل تلك المواد الرخيصة والمتوفرة في الطبيعة كمواد مائنة في العوازل الحرارية الخضراء، تخلق فائدة كبيرة لاقتصاد دولة الإمارات العربية المتحدة وهذا يعد تأثير رئيسي على هذه الدولة.

**مفاتيح البحث الرئيسية:** العوازل الحرارية الخضراء، مركب، بولي لاكتيك اسيد، المخلفات الطبيعية، خشب النخل المطحون، بذور التمر المطحون.
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Dedication

To my beloved parents, family and friends
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<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>Cp</td>
<td>Specific heat capacity</td>
</tr>
<tr>
<td>DPP</td>
<td>Date pit powder</td>
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<tr>
<td>DPWP</td>
<td>Date palm wood powder</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>E</td>
<td>Compressive modulus</td>
</tr>
<tr>
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<tr>
<td>$\Delta H_c$</td>
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<td>k</td>
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<td>Scanning Electron Microscopy</td>
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<tr>
<td>$T_m$</td>
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<td>Crystallization temperature</td>
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<td>$T_g$</td>
<td>Glass transition temperature</td>
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<td>Underwriters Laboratories</td>
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<tr>
<td>$W_f$</td>
<td>Weight of specimen after immersion</td>
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<td>$W_i$</td>
<td>Weight of specimen before immersion</td>
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<tr>
<td>$W_{matrix}$</td>
<td>Weight of PLA</td>
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<td>$W_{filler}$</td>
<td>Weight of DPWP or DPP</td>
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<td>Water Retention</td>
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<tr>
<td>$X_c$</td>
<td>Degree of crystallinity</td>
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<td>$\rho_{\text{composite}}$</td>
<td>Density of composite</td>
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<td>$\rho_{\text{matrix}}$</td>
<td>Density of PLA</td>
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<td>$\rho_{\text{filler}}$</td>
<td>Density of DPWP or DPP</td>
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<td>$\alpha$</td>
<td>Thermal diffusivity</td>
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<tr>
<td>$\sigma_u$</td>
<td>Compressive strength</td>
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<tr>
<td>$\sigma_y$</td>
<td>Yield strength</td>
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<tr>
<td>phr</td>
<td>Parts per hundred rubber</td>
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<td>wt.%</td>
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Chapter 1: Introduction

1.1 Introduction

There are many diverse sources of global environmental problems, such as ozone depletion in the stratosphere, soil degradation and the greenhouse effect. Perhaps, the most serious environmental problem in relation to energy use is that caused by climate change. Greenhouse gases such as carbon dioxide (CO$_2$), carbon (C) and chlorofluorocarbons (CFCs) trap heat from the earth’s surface, and thus increase the temperature of earth’s surface. Nowadays, CO$_2$ emissions contribute for approximately 50% of the anthropogenic greenhouse effect [1].

Starting with the Industrial Revolution, the concentration of CO$_2$ has increased by nearly 30% in the last 200 years because of man-made CO$_2$ emissions [2]. According to the National Oceanic and Atmospheric Administration (NOAA) CO$_2$ level have reached 409 ppm [3], see Figure 1 [3]. The pollution caused by these emission increases as energy consumption continues to rise. From an environmental perspective, buildings create more than $\frac{1}{3}$ of global greenhouse gas emissions, in the developed and developing countries [4]. Energy saving strategies and more efficient energy use could reduce these emissions substantially, however, practices such as space heating and cooling are a major factor related to energy consumption in buildings, see Figure 2 [5].

The residential sector is a key energy consumers as many buildings use a great deal of energy due to poor thermal insulation properties found in many existing building materials [6, 7]. In fact, ~40% of total world energy use in 2014 was consumed by buildings [8]. At present, residential buildings account for more than 25% of total...
energy using in Europe, with the trend estimated to rise over the coming years [4]. By 2015, electricity using in the UAE had reached to 126.6 billion kWh [9] with an additional expected annual increase of 9%. In addition, UAE is one of the highest energy consumption per capita [10], with demand growing at 10% per annum [11]. Therefore, saving or reducing energy consumption is vitally important due to high energy prices, the gradual depletion of fossil fuels and a rising awareness of environmental cases.

![Figure 1: Profile of atmospheric CO₂ concentration](image)

These days, we have many traditional materials for thermal building insulation, such as polyurethane (PUR) and expanded polystyrene (EPS). These materials exhibit good thermal conductivity values of between 0.03-0.06 W/m.K [7]. However, from a mechanical strength perspective, these materials have poor mechanical properties, which can limit their application in construction processes [12]. In addition, the
thermal conductivity values of other building materials are usually higher than the values found in traditional thermal building insulation materials. For example stainless steel has a value of 17 \( \frac{W}{m \cdot K} \), aluminum is 220 \( \frac{W}{m \cdot K} \), concrete (0.15–2.5) \( \frac{W}{m \cdot K} \), brick (400–800) \( \frac{W}{m \cdot K} \), stone (1–2) \( \frac{W}{m \cdot K} \) and glass at 0.8 \( \frac{W}{m \cdot K} \) [7]. It should be noted that currently there are no thermal building insulation materials without some drawbacks.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity ( \frac{W}{m \cdot K} )</th>
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</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>17</td>
</tr>
<tr>
<td>Aluminum</td>
<td>220</td>
</tr>
<tr>
<td>Concrete</td>
<td>0.15–2.5</td>
</tr>
<tr>
<td>Brick</td>
<td>400–800</td>
</tr>
<tr>
<td>Stone</td>
<td>1–2</td>
</tr>
<tr>
<td>Glass</td>
<td>0.8</td>
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</tbody>
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It should be noted that currently there are no thermal building insulation materials without some drawbacks.

![Figure 2: Building energy consumption (2019) in buildings](image)

Poly Lactic Acid (PLA) is a thermoplastic polymer derived from renewable raw materials, such as cornstarch. It is both biodegradable and compostable. PLA’s applications include uses in packaging and in manufacturing medical devices. It can also be easily processed on standard plastics equipment in order to produce molded parts, film or fibers [13]. PLA has the potential to serve as a useful insulation material. However, there is one case that needs to be addressed. That is the relatively high
manufacturing cost of PLA compared to conventional petro-chemical-derived polymers. That said, increased production of PLA in recent years has lowered its cost [14].

This study investigates the properties of PLA, and its composites, in order to provide insights into the development of heat insulator composites based upon biodegradable polymers. By incorporating certain fillers into a PLA matrix, thermal conductivity can be reduced, and the cost lowered by adding low-cost reinforcements. Date palm waste, such as date palm wood and date pits have been utilized in this study to reinforce the PLA matrix to prepare thermal insulation composites.

Date pits (DP) and date palm wood (DPW) are available in a number of countries. They have typically been viewed as a waste product from the date harvest and are usually discarded. The goal of this study is to find a material, or composite, that has low thermal conductivity, that reduces electricity consumption and, consequently, reduces carbon emissions. Therefore, the cost of the filler should be lower than the cost of the PLA.

In this thesis, composite materials using both PLA and date palm waste (DPP and DPWP) were prepared by a melt extruder system and compression molding machine (hot press). Then the composites were subjected to different thermal, physical, and mechanical tests to optimize performance.

1.2 Relevant Literature

More than 99% of global plastics are derived from petrochemicals. Such petroleum plastics are versatile, lightweight, flexible and relatively inexpensive. Nevertheless, with increasing environmental awareness and mounting ecological risks,
such as millions of tons of plastic packaging going into landfill yearly or harming wildlife, finding alternatives is an increasing urgent concern. These environmental issues are strong motivators for scientists and governments to reach alternatives to petro-based polymers. Therefore, there has been an increasing focus on bioplastics, whether partially or fully bio-based, biodegradable, or both, in order to find a solution to this problem [15, 16].

Furthermore, as buildings increase their energy consumption and emit more carbon the environmental issue becomes even more pressing. As such, we should seek to control heat flow in homes by using insulation. Consequently, heating and cooling expenses will be reduced considerably by using efficient insulation materials.

1.2.1 Renewable (biodegradable) polymers

Every year, the market for biopolymers grows and new demands can be predicted for applications that offer clear benefits to customer and are environmentally friendly. A 2016 report by BCC Research estimated global bioplastic totals in 2015 at 1.6 million metric tons, with a predicted increase to almost 6.1 million metric tons in 2020. This represents a compound annual growth rate (CAGR) of 30% for the 5 years interval from 2015 to 2020 [17]. See Figure 3.

The concept of ‘biopolymers’ does not have one universally recognized definition, but is generally accepted to be; (a) based on renewable and biodegradable resources; (b) also based on renewable resources that are not biodegradable, and; (c) based on fossil fuel resources that are biodegradable [18].
Therefore, our focus will be on polymer-based renewable and biodegradable resources. In this case poly lactic acid (PLA).

Biodegradable polymers are derived from renewable sources such as starch, or biodegradable synthetic polymers like polyesters from petroleum. Aliphatic and mixed aliphatic/ aromatic polyesters or polysaccharides (cellulose and its derivatives; particularly starch) are the most widely studied biodegradable polymers [19].

**1.2.1.1 Poly Lactic Acid (PLA) structure and preparation**

PLA is a biodegradable polymer derived from renewable raw materials such as cornstarch and sugarcane. It is used in many areas such as medicine for bone fixation and controlled drug release. It is also used for packaging, compost bags and sustained release systems for pesticides and fertilizers [20, 21]. PLA is a thermoplastic, high-strength and modulus polymer that can be made from renewable resources to produce many varied components for use in biocompatible/ bio-absorbable medical instrument market or the industrial packaging field. It is simply processed on standard plastic to produced molded parts, film, or fibers [21].
In addition, PLA is non-toxic, non-tissue reactive and biodegradable. Neither the polymer itself nor the by-products of its degradation are retained in any vital organs. It is suitable for vascular grafts and other surgical implants [22]. Therefore, PLA is an eco-friendly product with many advantages compatible with use in the human body (i.e. non-toxicity) [21].

Currently, there are two major methods for producing PLA on an industrial scale [18]. In both cases, lactic acid serves as the feedstock for PLA production.

a) Direct polycondensation of lactic acid (LA), see Figure 4 [23].

b) Ring-opening polymerization (ROP) via a cyclic dimer (lactide), see Figure 5 [24].

![Figure 4: Lactic Acid](image)

PLA can be categorized into two groups [25]: L-PLA and DL-PLA which are crystalline and amorphous respectively in most cases. DL-PLA is more sensitive to hydrolysis, while L-PLA is highly resistant to hydrolysis. In fact, PLA is used in copolymer form with these two isomeric monomers. The structural formula of PLA is shown below, see Figure 6 [25].
Nature Works LLC is a pioneer to manufacture the PLA with different grade based on several characteristics such as the L: D ratio [18], but currently, there are other manufactures, for example Palgreen (Mitsui Chemicals Tohcello, Japan), and Zhejiang Hisun Biomaterial (Zhejiang, China) have been known to produce PLA [26].

PLA is an example of commercially available biodegradable polymeric materials. It used in the field of composite manufacturing [27]. In addition, it became one of the most widely used polymers in the market because of its useful properties.
ways in which PLA can be reinforced have been covered in the literature in recent years.

1.2.2 Poly Lactic Acid (PLA) composites

PLA is the initial product polymer to be manufactured from annually renewable resources. It is categorized as generally known as risk-free (GRAS) by the United States Food and Drug Administration (FDA) and is considered safe to use as the packaging of the food. As a result of FDA approval, research on lactic acid-based polymers and their medical applications has accelerated considerably over the past 20 years, which have also seen the increased use of large-scale industrial lactic acid-based polymers for other uses [21, 25].

In the medical arena, PLA is used widely in tissue engineering and drug delivery procedures. These medical applications can be divided into three general categories: temporary implants, permanently implanted devices, and extracorporeal applications [30].

The most convenient and compliant means of patient treatment is controlled drug delivery strategies. The rapid improvement in biotechnology has resulted in the large scale production and synthesis of biomolecules that have shown their potential to deal with numerous health issues. Such biotechnology has many applications in terms of diagnostics and time-sensitive analysis [31, 32].

Tyler et al. [32] focused on three things in their research paper: the defiance to biomolecule delivery; classical approaches to PLA based biomolecule delivery, and the targeting strategies that were being developed and trialed. The found that the biological nature of these drugs, and molecules, posed significant challenges in terms
of navigating around the native defense mechanisms of the human body. They were characterized as having high levels of susceptibility to hydrolysis, enzymatic degradation and a short in vivo half-life that required more frequent dosages.

Moreover, PLA involves new biomaterials. Tanase and Spiridon [33] designed and evaluated new composites consist of PLA with chitosan and keratin were gained via a blended preparation. Their aim was to investigate the mechanical and in-vitro behavior. The founding pointed to composites with an increased young modulus, and a good uptake of surface properties. In addition, a significant improve in hardness, and decreased tensile strength. Biological assessments, using a human osteosarcoma cell line, indicated a good viability/proliferation outcome. Finally, these results indicate that composites might have prospective applications in the field of medicine.

Damadzadeh et al. [34] studied how a ceramic filler effect on the thermal and mechanical behavior of PLA and poly-L-lactic-co-glycolic acid composites in medical applications. In this study, the mechanical strength and thermal properties of the composites were examined. The composites were produced through an extrusion compounding process that gave 22.5 mm diameter-sized profiles. The results suggested that the thermal stability of the composites was rational. Moreover, SEM detect that these fillers were well sparse in the matrices and that mechanical properties were improved by adding the fillers. In addition, the modulus increased from 3.3 to 4.6 $GPa$ by adding filler particles (30 wt. %), while the flexural strength was decreased from 133 to 106 MPa.

The current trends in biodegradable polymers indicate new developmental strategies and engineering innovations designed to produce polymeric materials of great interest to both the industrial and academic fields. It has been identified that
incorporating functional fillers into the PLA matrix can enhance its thermal and mechanical properties and improve the surface characteristics of the matrix that are most important medical field like tissue engineering and artificial bone reconstruction.

The tanning industry produces a lot of waste. Olivares et al. [35] prepared PLA composites from keratin fibers derived from tannery waste. See Figure 7 [36]. These composites were prepared using melt-extrusion techniques. The process used two different materials to compound the PLA. These were KFs with differing content, and KFs combined with a traditional flame retardant such as aluminum trihydroxide (ATH). The PLA composites were studied via SEM and through a thermogravimetric analysis (TGA) under nitrogen and air. They were also investigated by using UL94 classification, dynamic-mechanical, mechanical and rheological measurement. This helped to identify a suitable KF/polymer matrix adhesion. It was seen that tenacity increased by 66%, tensile strength by 16%, and breaking strain by 40, when the ATH content was reduced from 50 phr to 30 phr in combination with a 3 phr KF content. Rheological measurements were used in simple and oscillatory shear flows and appeared that KFs reduced viscosity and thus improved the processing capabilities of the composites (phr = part by 100 of rubber).

This research provided solution to various problems where waste was used as a fiber that could improve PLA. It helped to overcome any negative impact that KFs cause to the environment, as well as enhancing PLA that could be used in automotive fields, electrical and electronic. This includes flame retardant panels, cabinets or protective housing.
Figure 7: Tannery industry

Wang et al. [37] have reported on versatile and an environmentally friendly method to produce ultra-low-threshold and lightweight biodegradable polylactic acid (PLA)/ MWCNT (Multi-Walled Carbon Nanotube) foam with high performing thermal insulation and EMI shielding applications. The three-dimensional conductive MWCNT networks embedded in the fine microcellular PLA matrix created excellent EMI shielding performance, with an EMI SE of up to 45 dB and a specific EMI SE of as high as $1010 \, dB \cdot cm^3 \cdot g^{-1}$. It also displayed superb thermal insulation with thermal conductivity of as low as $27.5 \, mW/(m.K)$.

Furthermore, Ameli et al. [38] found that low-density PLA composite foams had improved rigidity, were ductility impact resistant, whereby using a high pressure foam injection molding (HPFIM) process could improve their thermal conductivity. This process is useful in the transportation and construction industries. They used talc and nano-clay as a filler with 5 wt. %. The manufacture of high void fraction PLA, and PLA composite foams increases specific impact resistance (up to 15%) and
ductility, improves flexural rigidity (up to four times, and enhances thermal insulation (up to three times). Indeed, introducing 30% void fraction by regular foam injection molding FIM decreased the thermal conductivity of the injection-molded PLA, PLA/talc, and PLA/clay samples from 0.25 $W/(m\cdot K)$ to almost 0.15 $W/(m\cdot K)$, while introducing an approximately 65% void fraction. Using FIM with a mold opening reduced the thermal conductivity to about 0.09 $W/(m\cdot K)$.

In other areas, endeavors to diminish the weight and cost, just as improving the sustainability of automobile, have led to more research on alternative sustainable materials in the vehicles industry. Natural fiber strengthened polymer composites have become top choice and have been widely used as interior and exterior materials carrying out various functions in vehicle manufacture [39].

Carbon-fiber reinforced polymer composites provide design engineers with longer life expectancy and excellent quality. Lower weight, less maintenance, and higher strength have led to its use in many engineering contexts, where such composites are increasingly used to replace metals in a number of industrial, sporting and transport applications [40, 41].

Li et al. [42] manufactured a continuous carbon-fiber reinforced PLA composite by using three-dimensional (3D) printing. Their experiments compared printed samples with, and without, preprocessed carbon-fiber bundles. They measured the thermodynamic properties and mechanical strength with an electronic testing machine and a dynamic mechanical analyzer (DMA). They also used a novel nozzle and path control method to satisfy the demands of continuous carbon-fiber printing. The experiment and analysis showed that preprocessed carbon-fiber with a PLA sizing agent could effectively increase the interfacial strength exhibited between carbon-fiber
and PLA resin. They argued, based on their results, that the flexural strength and tensile strength of the modified composites with carbon-fiber reinforced were 13.8% and 16.4% higher than the original carbon-fiber reinforced samples. SEM examine outcomes pointed out that the appropriate bonding interfaces were constituted of a customized carbon-fiber reinforced PLA composite.

Additionally, this technology offers the possible technology to fabricate complex as well as high-performance composite elements, especially for complex airplanes structures [42].

1.2.2.1 PLA/natural fiber composites

In fact, you will find a swift growth in using natural waste in place of traditional fibers as reinforcements in composite material [43, 44]. As a result of a rise in environmental awareness, the matter for environmental sustainability along with the rising problem of global waste, natural waste fibers have been accustomed to strengthening thermoplastics. Generally due to characteristics such as low price, biodegradability, renewability, appropriate specific strength, and good thermal insulation properties [45, 46].

Porras and Maranon [47] prepared laminal composites based on PLA and bamboo fabric. These laminate composites were generated by applying a film stacking technique. The thermal, physical, and mechanical properties of the bamboo fabric, the PLA matrix, and the laminate composites were inspected. They obtained that the mechanical attributes were greatly improved. In addition, a SEM evaluation of these laminate composites exhibited a good bond between the bamboo fiber and PLA matrix.

In brief, laminated composites based on PLA and bamboo fabric displayed outstanding
energy absorption capabilities which could be utilized in structural engineering applications.

The performance of fiber reinforced in composites depends on many factors. Pickering and Efendy [48] worked on the structure and mechanical behavior of PLA supported by aligned discontinuous alkali treated natural fiber mats. The new feature of this study was regarding composite processing along with the utilization of fiber mats to establish a dynamic sheet former (DSF) where discontinuous treated fibers were aligned. Composites with various fiber weight content were tested with optical microscopy, SEM and tensile examination. It was found that their mechanical properties increased. For example, the tensile strength of harakeke and hemp composites enhanced by around 101.6 MPa and to 87.3 MPa respectively. This was roughly 90% and 60% greater than for PLA alone (53.9 MPa).

A natural and low cost filler can be got by grinding the culms of arundo donax. See Figure 8 [49] This has been used to prepare PLA-based bio composites by Fiore et al. [50]. They worked on preparing composites by melting PLA compounded with an arundo donax filler (ADF). Afterwards, the effect of the content and size of the ADF on morphology, and on the thermal and mechanical properties of PLA–ADF composites were investigated. The results indicated a significant effect due to additional ADF for all the properties investigated, especially when the ADF content was increased.
Couture et al. [51] investigated the mechanical properties of composites consisting of PLA as matrix with two types of unidirectional flax composite, where one made with layers of aligned flax rovings alone, and the other containing an additional paper layer. They noticed that the mechanical properties were promising for the industrial applications of this new kind of reinforcement.

Chen et al. [52] attempted to improve the crystallinity, mechanical properties, and heat resistance of PLA composites by chemically functionalized reinforcement, for example utilizing kenaf fibers (KF) and also multi-walled carbon nanotubes (MWCNTs). They performed a DSC examination and observed that functionalized KF can accelerate crystalline growth and raise crystalline content. The DSC outcomes as well revealed that annealing treatment further drove PLA re-crystallization, and improved crystallinity. Furthermore, the Avrami Equation showed that functionalized KF and MWCNTs are beneficial in transforming PLA crystallinity from a 3-dimensional bulk (or spherical) structure into a 2-dimensional sheet structure.
Sutivisedsak et al. [53] developed new utilizes for agricultural by-products as well as waste products in order to promote green chemistry and find applications with greater values. They assessed cotton byproducts as fillers for PLA and low-density polyethylene LDPE. They applied melt-blending and extrusion to create polymeric composites based on the cotton burr and cotton seed bull. They arrived at that the addition of these fillers somewhat changed the composites’ thermal characteristics, but to a great extent minimized the composites’ mechanical properties. Thereby, PLA-filler composites may very well be useful for reducing the price of materials in applications that can tolerate these minimized properties. Besides, the addition of fillers to LDPE could be useful in applications that enhance rigidity or biodegradability.

Koutsomitopoulou et al. [54] focused on recycling olive pits. See Figure 9 [55]. Olive pit powders were first characterized then, added to a bio-based and biodegradable matrix (polylactic acid, PLA) at various percentages. After grinding (both planetary milling and centrifugal methods were used), a comparison of size was made based on the distribution and densities of the olive pit powders. The results revealed an increase in tensile modulus, but flexural strength decreased due possibly to poor interfacial bonding between the olive pit powder and the PLA.
Anwer et al. [56] compared PLA-Lignin and PLA-Tannin composites by characterizing their mechanical, dynamic-mechanical, and thermal properties. They used injection molding to produce composites with varied wt% (5, 10, and 15) of filler in the PLA. During their research, they recorded the different effects on the properties of PLA. For example, SEM morphology detected lignin droplet like dispersions within the PLA matrix when contrasted with tannin. The particle size of the lignin in the matrix was 10-150 times lower than the tannin. Isothermal frequency sweeps explained that the storage modulus of the PLA-tannin composites began to degrade at 15 wt% of filler concentration and damping increases. PLA-lignin composites do not display a similar degradation in the storage modulus. Additionally, the tensile strength of the two PLA-lignin, as well as PLA-tannin composites, turned down with an increase in filler content. Lignin has a more inhibitory impact on PLA crystallization as compared to tannin. Lastly, the onset of thermal degradation of the PLA-lignin and PLA-tannin composites took place at slightly reduced temperatures than with pure PLA.

Le Guen et al. [57] assessed the possible of farm dairy effluent (FDE) in the form of a filler in the PLA. The integration of FDE in the PLA was studied and compared with wood sanding dust (SD). They applied the two extrusion and injection molding techniques. Consequently, the mechanical and thermal properties of the injection molded specimens were assessing as a function of the filler sort. This examination pointed out that FDE had an equivalent density to SD however lower rigidity because of the appearance of proteins along with a smaller quantity of cellulose. Furthermore, Young’s Moduli of FDE composites were greater than for the pure PLA, where the tensile strength usually reduced, but still continued to be comparable to those filled with SD. Besides, the FDE composites degraded at least 2 times as rapidly as the pure PLA and SD composites. This is likely due to the acids
(e.g. fatty and amino-acids) present in FDE but not contained in SD. Finally, they proposed that FDE has possible as a composite filler with enhanced stiffness and in light of a UV rapid degradation perspective.

The fillers can be customized to improve incorporation within PLA, which is able to have a positive impact on the properties of the composites. The physical and mechanical properties of the PLA composites strengthened by TiO$_2$ grafted flax fibers, were studied by Foruzanmehr et al. [58]. In their study, impact and tensile strength tests examined the mechanical properties of modified TiO$_2$ grafted flax fiber reinforced composites. To explore the thermal and thermo-mechanical attitude of the composites, DSC, TGA, and dynamic-mechanical analysis (DMA) were applied. Additionally, the hygroscopic behavior of the composites was determined by way of a water uptake assessment. The outcome of this work revealed a statistically tremendous increase in adhesion bonding by the modified fibers to the matrix. The modified TiO$_2$ grafted flax fibers increased the impact resistance of pure PLA by three times. The microscope observations verified modifications in the mechanical and physical properties of the composites. Moreover, the amount of water absorption decreased by 18% in the modified TiO$_2$ grafted fiber reinforced composite.

In same vein, Spiridon et al. [59] used cellulose fibers in preparing PLA/ fiber composites through an organosolv process. They treated the cellulose fibers chemically using stearoyl chloride also the enzyme laccase. The concluded that the inclusion of cellulose fibers to the PLA matrix was given a positive influence on some of the mechanical properties of the composites. Furthermore, thermal properties were enhanced, while rheological properties declined. Generally, these fiber modifications did not have the desired impact of bettering the mechanical properties any further,
while thermal properties viewed a substantial difference where chemically modified fibers were used. The behavior of PLA/fiber composites throughout accelerated weathering was also studied. The outcomes were compared to composites made using commercially available kraft pulp fibers.

Furthermore, Gordobil et al. [60] utilized spruce (softwood) and eucalyptus (hardwood) woods like raw substances for lignin extraction applying an organosolv process. Esterified lignin was used as filler in PLA film elaborated by solvent casting in various concentrations from 1% up to 50%. Afterward, the thermal, and mechanical water barrier properties of the prepared films were tested. The findings exhibited that the addition of modified lignin resulted in greater ductility and lower rigidity, thus offering plasticity to the PLA. In fact, PLA is a brittle and stiff polymer, which has an extremely low capability in terms of plastic deformation (~3%). This brittleness is one essential drawbacks of PLA [29]. Therefore, modified lignin used as a filler in different concentrations can overcome many of the major weaknesses of using PLA (e.g. brittleness and stiffness).

1.2.3 Natural fibers and date palm wastes

Natural fibers can be utilized as thermal insulation material. In fact, natural fibers are environmentally-friendly and renewable materials that have numerous advantages over synthetic fibers [61].

For example, Khedari et al. [62] used a mixture of durian peel and coconut coir to develop a new low-cost particleboard with lower thermal conductivity (0.1342 $W/(m.K)$). Their product made use of wall and ceiling insulation to save energy.
Other fillers such as corn cobs can be obtained from agricultural processes. Corn cobs have been used as wall insulation in the past [63]. Pinto et al. [64] came to the conclusion that there were considerable similarities between corn cobs and extruded polystyrene with regards to microstructure as well as chemical composition. Consequently, they noticed corn cobs as a sustainable construction material with good thermal insulation properties.

Other researchers have worked with other fibers in order to investigate their thermal insulation properties and use them for building purpose. For example Zhou et al. [65], Xu et al. [66], Zach et al. [67], and Sahari et al. [68].

1.2.3.1 Date palm waste

Date palms are available in a number of countries, and are common in Gulf Cooperation Council (GCC) countries. The United Arab Emirates has about 40 million date palms, more than three-quarters of them are in Abu Dhabi Emirate. Each palm generates about 15 kilograms of biomass waste annually. Date palm wood and date pits are date palm waste which could be a problem for municipal waste management. However, solutions to these waste management problems can be both creative and sustainable.

Agoudjil et al. [69] studied the possibility of using date palm wood (DPW) as thermal insulation for buildings. Three sorts of date palm wood (leaf base, petiole and bunch) were examined in the Biskra oasis in Algeria. They noted the outcomes of an experimental investigation on their thermophysical, chemical and dielectric properties. The results showed that DPW is a good source for formulating efficient and safe insulation materials rather than the other natural materials.
In addition, Benmansour et al. [70] prepared composites consisting of natural cement, sand and DPW. The aim was to investigate the chance of using this material as a component of insulating materials as a way to decrease heat loss in buildings. The outcomes revealed that as the DPW content raised (5%, 10%, and 15%) the thermal conductivity minimized and thus provided a composite with good thermal and mechanical properties which could well be served in the construction industry as a bio-composite, energy efficient building materials.

Masri et al. [71] used date palm leaflets waste as a reinforcement for EPS waste, dissolved in gasoline to be able to create composites. They performed, thermal, mechanical, physical and morphological measurements to describe leaflets-polystyrene composite (LPC). According to their results, they concluded that date palm waste is well suited to the formulas of efficient as well as safe insulating materials when compared to a number of other natural materials.

Other investigations have examined date wood and date pits as thermal insulation materials. Abu-Jdayil et al. [72] produced a composite material made of unsaturated polyester with date-pits or date palm wood as a filler. The purpose was to function as an insulating material. The outcomes revealed that the date wood-based composites functioned better than the date pit composites. Nevertheless, they reported that the thermal conductivity of both composite materials was highly promising and very similar to many commercial thermal insulators.

Alsewailem et al. [73] investigated the compatibility of two types of date pit (DP), from Saudi Arabia, with polystyrene (PS) and high-density polyethylene (HDPE). They tested the thermal and mechanical properties of these composites. They got that; the mechanical properties were decreased when the date pit content increased
in the composite. However, composites of sekari (S) date pits displayed higher mechanical properties than those containing khlaas (K) date pits. Moreover, the addition of date pits, no matter what kind (either K or S), tended to decrease the heat of the fusion of the HDPE/ date pit composites at a larger date pit content ratio, >10 wt. %.

Moreover, Almi et al. [74] studied eight varieties of date palm residue as a potential composite reinforcement. They reported on their mechanical properties and thermal behavior. Their outcomes prove that the rachis variety displayed relatively greater values of tensile strength and Young’s Modulus. In contrast, the petiole variety shown relatively large values for specific mechanical properties. In addition, the results of the thermal analysis revealed that the leaflets variety produced the maximum resistance to thermal degradation, as its degradation only happened at 360 °C. Generally, the TGA of these date palm residues pointed out that date palm fibers were perfect as a reinforcement to create composites, even with thermoplastic matrix materials whose processing temperature was lower than 320 °C.

The possibility of using date palm wood and date pits in composite manufacture will help start new markets for what is commonly known to be a waste or low value product. Therefore, from an economic perspective, the accessibility to these fillers, typically of agricultural origin, at very low cost, makes production of these composites economically practical.
Chapter 2: Materials and Research Methods

2.1 Materials

2.1.1 Poly lactic acid

The semi crystalline PLA 4032D used in this research was supplied by Zhejiang Zhongfu Industrial Limited, Zhejiang, China. PLA (4032D) was supplied in pellet form with an L-lactide:D-lactide ratio from 24:1 to 32:1 as reported by the manufacturer, and a molecular weight of 2.41X10^5 g/ mol [75]. The specific gravity of the PLA is 1.24, and its melting point varies between 155-170 °C. Moreover, it has the highest heat capacity among polyester plastics [76]. The average diameter size of the PLA pellets is 3.5 mm, see Figure 10.

![Figure 10: Pure PLA (4032D)](image)

2.1.2 Date palm wood powder (DPWP)

The date palm wood used in this study was obtained from the UAE University farm in Al Foah, UAE. The date palm wood was dried for one week in order to be rid of any moisture. After that, it was crushed and ground using a commercial milling machine (Figure 11) and then it was sieved. Only date palm wood powder (DPWP)
Particles less than 212 μm in size were used to produce the composite samples. The particle size distribution for the DPWP is shown in Figure 12.

The DPWP consisted mainly of three mixed parts (leaflet, rachis, and fiber) according to the supplier. An analysis of the main components (cellulose, hemicellulose and lignin) is presented in Table 1 [77]. The analysis was carried out by another research group in one of our laboratories by using Klason Method.

Figure 11: Date palm wood component
Figure 12: Date palm wood particle size distribution

Table 1: Composition of date palm biomass

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element Analysis (ppm)</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>26.3±0.4</td>
</tr>
<tr>
<td>P</td>
<td>12.0±0.4</td>
</tr>
<tr>
<td>Ca</td>
<td>166.6±12</td>
</tr>
<tr>
<td>Mg</td>
<td>21.2±2</td>
</tr>
<tr>
<td>Na</td>
<td>9.3±1.6</td>
</tr>
<tr>
<td>Hemicellulose (wt. %)</td>
<td>14.8±1.2</td>
</tr>
<tr>
<td>Cellulose (wt. %)</td>
<td>30.2±1.2</td>
</tr>
<tr>
<td>Insoluble Lignin (wt. %)</td>
<td>25.4±1.0</td>
</tr>
<tr>
<td>Soluble Lignin (wt. %)</td>
<td>1.0±0.0</td>
</tr>
<tr>
<td>Ethanol-Benzene Extractives (wt. %)</td>
<td>16.0±2</td>
</tr>
</tbody>
</table>
2.1.3 Date pit powder (DPP)

The date pits used in this study were obtained from the UAE University farm in Al Foah, UAE. The date pits were dried for a week to get rid of any moisture and were then crushed using a commercial milling machine (Figure 13) before being sieved. Only DPP particles less than 212 μm were used to produce the composite samples. The particle size distribution is shown in Figure 14.

The DPP waste used in this research is widely available in the UAE, with many facilities producing this waste such as the Al Barakah Dates Factory, Emirates Dates Factory and the Sharjah Dates Factory. This DPP is from palms and its main components are cellulose, hemicellulose and lignin. The DPP has not undergone an analysis yet should still give results close to the DPWP analysis shown in Table 1. Generally, the percentages of hemicellulose, cellulose, and lignin content are 25-30, 35-50, and 10-30 wt. %, respectively [78].

2.1.4 Chemicals

Sodium Hydroxide (\(NaOH\)) with a molecular weight of 40 g/ mol was obtained from Sigma-Aldrich, and citric acid (\(C_6H_8O_7\)) with a molecular weight of 192.112 g/mol was supplied by Alpha Chemicals.
2.2 Fabrication of composite samples

2.2.1 Molds

Different tests, such as thermal, chemical, physical and mechanical were conducted. For all these test, different molds were made from a stainless-steel base corresponding to ASTM standards. The thermal conductivity mold was produced by Al Safa Engineering and Contracting Workshop, while the Bin Moses Workshop provided the compression and fire test molds. Both companies are located in Al Ain, UAE. See Figure 15.
2.2.2 Fabrication of Pure PLA samples

As PLA is sensitive to hydrolysis at high temperatures in the presence of humidity [79], the PLA was dried for two hours under a vacuum at 90 °C and then moved to a desiccator for an hour prior to processing. An internal mixer, a mini-twin conical screw extruder (MiniLab Haake Rheomex CTW5, Germany) was used to melt the PLA. The melting was carried out at 190 °C and 140 rpm for 3 minutes with a batch size of 5 g. The screw length and screw diameter were 109.5 mm and 5/14 mm conical, respectively. The paste of pure PLA was shaped into two different types of mold, one for the compression test and the other for the thermal conductivity test. After that, the molds were placed in a compression molding machine (hot-press) where the test shapes were prepared. To avoid the samples from sticking to the mold, it was coated with a Maximum Mold Release Wax.

For the compression test samples, the heating cycle chosen to get rid of voids, consisted of three segments with different parameters: (1) a force of 0.5 tons at 180 °C for 16 minutes; (2) a 0.52 ton force at 185 °C for 10 minutes; and (3) 3 tons of force at 100 °C for 3:30 minutes. The heating cycles related to the thermal conductivity
samples included three segments also: (1) a force of 0.5 tons at 180 °C for 5:20 minutes; (2) a 0.52 ton force at 185 °C for 4 minutes; and (3) 3 tons force at 100 °C for 3:30 minutes. After that, the molds were put in an oven at 95 °C in order to pass through an annealing processing where the changes that might occur to the PLA in the annealing process could be studied. This was the first stage of this research. Figure 16 shows photographs of the compression samples (B) and the thermal conductivity sample (A) before testing.

Figure 16: Thermal conductivity & compression test specimens

These samples were collected in bags and labelled, using the abbreviation <interval>-<matrix name>. For example, ‘1-PLA’ sample is a one hour interval of the matrix PLA. See Table 3.

2.2.2.1 Annealing processing for pure PLA samples

The thermal treatment (annealing processing) was carried out in an oven at 95 °C. It was predicted that most polymer annealing process changes would occur in a range between the melting temperature (Tm) and the glass transition temperature (Tg) [80, 81]. However, PLA has a melting temperature of about 155 -170 °C [82] and Tg has one of less than 70 °C [18]. Thus, the temperature of 95 °C was chosen to avoid
melting the polymer chains. The annealing intervals were as following: fast, 0.5, 1, 3, 10, 17 and 24 hours for the first phase of the research. They were chosen thus in order to recognize how the annealing process effects thermal and mechanical properties. The composite samples underwent the annealing process for 3 hours at 95 °C to produce optimum thermal insulation properties.

<table>
<thead>
<tr>
<th>Annealing processing interval</th>
<th>PLA (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>100</td>
</tr>
<tr>
<td>0.5 hrs.</td>
<td>100</td>
</tr>
<tr>
<td>1 hr.</td>
<td>100</td>
</tr>
<tr>
<td>3 hrs.</td>
<td>100</td>
</tr>
<tr>
<td>10 hrs.</td>
<td>100</td>
</tr>
<tr>
<td>17 hrs.</td>
<td>100</td>
</tr>
<tr>
<td>24 hrs.</td>
<td>100</td>
</tr>
</tbody>
</table>

### 2.2.3 Fabrication of Composites

The PLA was dried for two hours under a vacuum at 90 °C and then moved to a desiccator for an hour prior to processing. An internal mixer, a mini-twin conical screw extruder (MiniLab Haake Rheomex CTW5, Germany) was used to melt the pure PLA and mix the DPWP or DPP with the pure PLA to prepare composite samples with different filler content (0, 10, 20, 30, 40, and 50 wt.%). The melting was carried out at 190 °C and 140 rpm for 3 minutes with a batch size of 5 g. After blending the paste was shaped into four different molds. After that, the molds were placed in the
compression molding machine (hot-press) where the test shapes were prepared. A release agent was used to prevent the specimens from sticking to the mold.

The compression test samples underwent the same heating cycles as the pure PLA. While the fire and thermal conductivity samples were exposed to the same heating cycles as the pure PLA’s thermal conductivity samples.

Table 3: Samples names and filler contents

<table>
<thead>
<tr>
<th></th>
<th>Annealing processing interval</th>
<th>PLA (wt.%)</th>
<th>DPWP/DPP (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-DPWP</td>
<td>3 hrs.</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>20-DPWP</td>
<td>3 hrs.</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>30-DPWP</td>
<td>3 hrs.</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>40-DPWP</td>
<td>3 hrs.</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>50-DPWP</td>
<td>3 hrs.</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>10-DPP</td>
<td>3 hrs.</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>20-DPP</td>
<td>3 hrs.</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>30-DPP</td>
<td>3 hrs.</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>40-DPP</td>
<td>3 hrs.</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

After this, the molds were put in the oven at 95 °C in order to complete the annealing process in three hours. The samples were collected in bags and labelled, using the abbreviation <weight percentage>-<filler name>. For example, '10-DPWP’ sample is a weighted percentage of 10 of the filler DPWP. See Table 3.
2.3 Measurements methods

2.4 Thermo-physical

2.4.1 Thermal conductivity

A thermal conductivity testing machine, Lasercomp FOX-200, was used to measure the thermal conductivity of the samples produced. A specific mold was produced according to the dimensions of the sample required by the Lasercomp heat flow instrument. The dimensions of the samples were 110 mm x 110 mm x 3 mm. See Figure 17. The measurement followed standard conditions and methods as reported by ASTM C1045-07. The steady state method was used in these measurements, where the thermal conductivity was determined from measurements of the temperature gradient in the sample and in the heat input. The average of these three samples is reported here.

![Figure 17: Thermal conductivity sample](image)

2.4.2 Differential Scanning Calorimetry (DSC)

This test was carried out for a closed system where the annealing process took place inside the DSC. A Differential Scanning Calorimeter Analyzer (TA Instruments 25DSC) was used to investigate the thermal properties of the extruded PLA, and the
composite samples. Approximately 5 to 7 mg of the particular samples were put into proper pans and sealed prior to installation into the heating cell of the DSC, under a nitrogen atmosphere at a flow rate of 50 mL/min. This test was done for two cases at each stage of the experiment.

**Pure PLA measurements**:

Case #1: The measurement started with heating samples to 200 °C with 40 °C/min and fixed them at 200 °C for 5 minutes to remove any thermal history. It was then cooled down to 95 °C with 5 °C / min and fixed at 95 °C for a specific interval (fast/ without stopping at 95°C, 30 mins, 1 hr., 3 hrs., 10 hrs., 17 hrs. or 24 hrs.) at each cooling step to carry out the annealing process. It was then cooled down to 20 °C with 5 °C/ min, after which the samples were heated from 20 °C to 200 °C with 2 °C/min.

Case #2: On one sample, the measurement was started with heating the sample to 200 °C with 40 °C /min and fixed it at 200 °C for 2 mins to remove thermal history, cooled down to 95 °C with 80 °C/min and fixed it at 95 °C for specific interval (fast "without stopping at 95°C", 5, 10, 20, 30, 40, 50, or 60 min ) for each cooling step to achieve the annealing processing, then cooled down to 20 °C with 80 °C/min, after that the sample was heated from 20 °C to 200 °C with 10 °C/min.

**Composite sample measurements**:

Case #1: This started with heating samples to 200 °C with 40 °C/min and fixed them at 200 °C for 5 mins to remove any thermal history. Then they were cooled down to 95 °C with 5 °C/min and fixed at 95 °C for 3 hours to complete the annealing
process. After that, they were cooled down to 20 °C with 5 °C/min, after which the samples were heated from 20 °C to 200 °C with 2 °C/min.

Case #2: For selected composites the standard ASTM D3418–03 [83] was followed, but the cooling rate was increased to 15 °C/min instead of 10 °C/min, and the rest time after the first heating was altered from 2 mins instead of 5 mins. In addition, this standard did not have the annealing process step.

The second heating scans were used to evaluate the material’s ability to crystallize and assess thermal glass transition temperatures (Tg) as well as other characteristics. In addition, the average specific heat capacity (Cp) of extruded PLA and its composites were measured. The measurements were carried out in a temperature range from 0 to 70 °C, with a heating rate of 3 °C/min. Average specific heat capacity values for the range from 20 to 40 °C were presented.

2.4.3 Water Retention

The water retention of the samples was measured in accordance with ASTM D570-98 [84]. Two specimens with dimensions of 25.7 mm in length and a diameter of 12.3 mm were prepared for each case (see Figure 18). All the specimens were dried in an oven at 80 °C for four hours and then moved to a desiccator to achieve a constant weight. They were also measured for initial weight (Wi). Then, the specimens were immersed in distilled water at either 23 °C or 50 °C for both the short and long term.

The short-term interval:

- For the first 24 hours. Every specimen was taken out and pressed dry with a cloth and weighed for up to 8-10 times.
• For the second 24 hours. Each specimen was weighed for up to 5-7 times.

• After that for a week, every specimen was taken out and pressed dry with a cloth and weighed once after each three days.

The long-term interval:

• A reading was taken weekly with the water at 23°C.

The amount of water absorbed by the specimen was calculated using equation (1). The values were reported in the average of two repetitions

\[ WR\% = \frac{W_f - W_i}{W_i} \times 100 \] (1)

WR (%) is the percentage of water retention by the specimen, and \( W_i \) and \( W_f \) [g] are the weights of the specimen before and after immersion in distilled water.

Figure 18: Water retention and compression test specimen

2.4.4 Density

The volume and the weight for the three specimens in each case were determined up to four significant digits in order to get an estimated density by dividing
the weight by the volume. The values were reported in the average of three repetitions. Also, the linear mixing rule was used to calculate the theoretical density of the prepared composites. Equation (2).

\[
\rho_{\text{composite}} = \left( \frac{w_{\text{matrix}}}{\rho_{\text{matrix}}} + \frac{w_{\text{filler}}}{\rho_{\text{filler}}} \right)^{-1}
\]  

(2)

Where \( \rho_{\text{composite}} \), \( \rho_{\text{matrix}} \) and \( \rho_{\text{filler}} \) are the densities of composite, PLA and DPWP or DPP, respectively. In addition, \( w_{\text{matrix}} \) and \( w_{\text{filler}} \) are the weight fraction of PLA and DWP or DPP.

### 2.5 Mechanical and Morphological Characteristics

#### 2.5.1 Compression test

The compression test was done in accordance with ASTM D695-15 [85]. Compressive strength, modulus and elongation at the break of the samples were measured by a universal testing machine (MTS model MH/ 20) with a load cell capacity of 100 kN. Three specimens with dimensions of 25.7 mm in length and a diameter of 12.3 mm were prepared for each case (see Figure 18). The specimen was compressed between the upper (moveable) and lower (fixed) plates of the machine. The loading continued either until a fracture occurred or the load value was reduced by 10% of the maximum load. Otherwise, the test was interrupted manually when a specific contraction value was reached. See Figure 19. All tests were conducted at room temperature and with an overhead speed of 1.3 mm/min. The average of three measurements was reported.
2.5.2 Scanning Electron Microscopy (SEM)

The examination of the PLA and fractured composites microstructure was carried out using a JEOL-JCM 5000 NeoScope Scanning Electron Microscope (SEM). The samples were installed on aluminum stubs and coated in gold to get rid of electrostatic charges throughout the examination in order to attain a maximum magnification of the textural and morphological features. Then images were recorded at different resolutions.

2.5.3 Fire testing

The UL94 flammability test was developed by Underwriters Laboratories to evaluate the physical characteristics and safety of different plastics when they are exposed to flame tests [86]. Samples with the following dimensions (125 mm in length, 13 mm in width and 4 mm thickness) were prepared according to UL94 V, which is the most commonly used test for measuring the ignition and flame-spread of vertical bulk materials exposed to a small flame (see Figure 20). UL94 V classifies the
materials as V-0, V-1 or V-2 according to vertical combustion. Figure 21 shows setup of the experiment [87].

![Figure 20: Fire testing (UL94 V) samples](image)

![Figure 21: Experiment setup](image)

A blue flame of 20 mm was exposed to the bottom of the sample and the top of the flame was 10 mm from the bottom edge of the sample. The following steps were required to carry out this test:
1) The flame is applied for 10 seconds and then it is removed. The after-flame time $t_1$, which is the time required for the flame to extinguish is recorded.

2) The flame is applied for another 10 seconds after initial extinction. The after-flame $t_2$, and afterglow $t_3$, the time required for the fire glow to vanish, are recorded.

Because of spillage, the burner should be tilted at a maximum angle of $45^\circ$ as in Figure 21. Table 4 represents the important related criteria [86].

<table>
<thead>
<tr>
<th>Fire classification</th>
<th>$t_1$ and $t_2$ less than 10 s for each specimen</th>
<th>$t_1 + t_2$ less than 50 s for the five specimens</th>
<th>$t_2 + t_3$ less than 30 s for each specimen</th>
<th>No after-flame or afterglow up to the holding clamp</th>
<th>No burning drops</th>
</tr>
</thead>
<tbody>
<tr>
<td>UL94 V$_0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UL94 V$_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UL94 V$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.5.4 Chemical resistance

Two chemical reagents were used; citric acid and sodium hydroxide solutions. 10 wt.% of citric acid and $NaOH$ solutions in distilled water were prepared to carry out this test according to the test standard ASTM D-543-84. Then, the same procedure as for the short term immersion water retention test was followed to study the chemical resistance of the composite.
The percentage of acid or base impregnation was calculated using Equation (3).

\[
\text{Acid or Base impregnation\%} = \frac{W_f - W_i}{W_i} \times 100 \quad (3)
\]

It is a measure for percent relative increase or decrease in weight of the solid matrix as a result of acid or base impregnation. The values were reported in the average of measured samples.
Chapter 3: Results and Discussion

3.1 Pure PLA

3.1.1 Thermo-physical properties

One of the important physical tests is the determination of density for the treated PLA specimens. Figure 22 presents the effect of annealing processing on the density of PLA samples.

![Figure 22: Density of PLA samples vs. annealing process at different times](image)

It can be seen that an increase in annealing time results in a slight increase in density. The density values are between 1232 $kg/m^3$ for the samples that were treated with fast cooling, to 1238 $kg/m^3$ for the samples that were treated with the annealing process for 24 hours. The increasing density was pointed in some papers where the density increased in line with an increase in the degree of the crystallization of the PLA [21, 88, 89].

Water retention was another physical test that can investigate the effect of the annealing treatment on the water absorption ability of the treated specimens.
Figure 23: Water retention results for PLA specimens

Figure 23 shows the water retention by the of PLA samples that had been exposed to the annealing process for different time periods at 95 °C. These specimens were measured for up to 8 days by immersing them in distilled water at room temperature. Starting in the first 48 hours (2 days) the percentage weight wt. % values were random. After that, for three days the specimens 0-PLA, and 3-PLA undergoing the annealing process showed a reduced reading and then the WR% increased slightly for the next three days. For the 24-PLA, the WR% increased continually for all six days. This indicates that the wt. % increases when the time allowed for the annealing process also increases (24hrs > 3hrs > Fast cooling).

Figure 24 shows the thermal conductivity of PLA for different treatment times in a temperature range of 5 °C to 50 °C.
Figure 24: Thermal conductivity for PLA at different cooling times in a fixed range of temperature

It is clear that the annealing process has an impact on the conductivity of the samples. For example, the thermal conductivity of 0-PLA is 0.06426 $W/m \cdot K$ at 25 °C, and the sample that had been annealed for 24 hours had a thermal conductivity of 0.09044 $W/m \cdot K$ at 25 °C. As a result, the annealing process has led to an increase in the thermal conductivity of the PLA samples, because the time of the annealing process allows for the spherulite to form comfortably and the crystals to be formed in a more orderly fashion, which does not impede heat transfer [81]. Figure 25 presents a 3D surface model of the PLA’s thermal conductivity at different times in the annealing process. The red color indicates a place with higher thermal conductivity.
Figure 25: 3D surface model showing dependence of thermal conductivity on temperature at different annealing process time

Thermal properties can be determined from the DSC, Table 5 summarizes some of the values from the Figure 26.

Figure 26: DSC results (Case #1)
Table 5: DSC results for PLA at different times of annealing process at 95 °C (Case #1)

<table>
<thead>
<tr>
<th>Interval (hour)</th>
<th>Tg (°C)</th>
<th>Tc (°C)</th>
<th>Tm (°C)</th>
<th>ΔHc (J/g)</th>
<th>ΔHm (J/g)</th>
<th>Xc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>53</td>
<td>89.9</td>
<td>168.4</td>
<td>19.2</td>
<td>50.6</td>
<td>33.8</td>
</tr>
<tr>
<td>0.5</td>
<td>57.6</td>
<td></td>
<td>168.7</td>
<td></td>
<td>48.8</td>
<td>52.5</td>
</tr>
<tr>
<td>1</td>
<td>56</td>
<td></td>
<td>168.6</td>
<td></td>
<td>47.7</td>
<td>51.3</td>
</tr>
<tr>
<td>3</td>
<td>56.4</td>
<td></td>
<td>168.5</td>
<td></td>
<td>50.3</td>
<td>54.1</td>
</tr>
<tr>
<td>10</td>
<td>57.6</td>
<td></td>
<td>168.8</td>
<td></td>
<td>54.5</td>
<td>58.6</td>
</tr>
<tr>
<td>17</td>
<td>56.6</td>
<td></td>
<td>168.3</td>
<td></td>
<td>60.3</td>
<td>64.8</td>
</tr>
<tr>
<td>24</td>
<td>59</td>
<td></td>
<td>169.7</td>
<td></td>
<td>54.3</td>
<td>58.4</td>
</tr>
</tbody>
</table>

Table 5 shows how the thermal properties are affected by changing the time of the annealing process for extruded PLA. The glass transition (Tg) increases at 0.5-PLA. Afterwards, the values vary from 56-59 °C. These values are within the ranges mentioned in the literature [21, 79]. In general, the PLA dependent on D-lactate contents and molecular weight exhibits a lower glass transition temperature (Tg) up to about 60 °C, as compared to polyesters (up to about 80 °C) [90, 91]. It can be deduced from this that the crystallization peak appears in fast cooling but only at 89.9 °C with an enthalpy of 19.2 J/g.

In addition, the melting point was 168 °C and it did not change when the annealing process time was altered. Enthalpy has a clear impact depending on the
different annealing intervals. The enthalpies were 50.6 J/g, 48.8 J/g, 47.7 J/g, 50.3 J/g, 54.5 J/g, 60.3 J/g and 54.3 J/g at intervals of: 0-PLA, 0.5-PLA, 1-PLA, 3-PLA, 10-PLA, 17-PLA, 24-PLA respectively. Moreover, the degree of crystallization has been calculated by equation (4). The effect of changing the intervals on the degree of crystallization was clear. Once the annealing process time increased, the degree of crystallization became higher. The highest degrees were for the highest intervals (10-PLA, 17-PLA, and 24-PLA) with 58.6%, 54.8% and 58.4% respectively, while for less than 10-PLA the degree of crystallization (%) was between 33.8% - 54.1%. See Figure 26.

\[
\%\text{Crystallinity} = X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^\infty} \times 100
\]  

(4)

Where \(\Delta H_m\) is the measured endothermic enthalpy of melting and \(\Delta H_c\) is the exothermic enthalpy that is absorbed by the crystals formed during the DSC heating scan. The theoretical melting enthalpy of 100% crystalline PLA was taken to be \(\Delta H_m^\infty = 93\ J/g\ [13]\).

![Figure 27: Degree of crystallinity at different times in the annealing process at 95 °C (Case# 1)](image-url)
A new approach checked how the thermal property changed in the same sample in one hour (Fast, 5min, 10min, 20min, 30min, 40min, 50min and 60min).

![DSC results (Case #2)](image)

Figure 28: DSC results (Case #2)

The glass transition reduced as the annealing interval increased. In general, the $T_g$ was low and in the range of 55.1- 49.1 °C. [90, 91]. Unlike in previous studies, there are three cycles of content crystallization, which peak at 92.9, 92 and 87.3 °C with an enthalpy of 32.5, 30.4 and 3.5 J/g respectively. These peaks indicate that when the annealing process is more than 10 minutes long it will crystallize more chains in the polymer.

Figure 28 shows the two peaks that are been shaped when the annealing process increases to more than 10 minutes at melting point. Although these separate peaks are clear up to 30 minutes, after that they decay and overlap. Also, it can be observed from the first ($T_{m1}$) and second fusion peaks ($T_{m2}$) that they move towards each other. The temperature ($T_{m1}$) at 10 minutes starts to increase from 152 °C to 153.3 °C, whereas the $T_{m2}$ starts to decrease from 167 °C to 162.1 °C.
Table 6: DSC results for PLA in one hour of the annealing process at 95 °C (Case #2)

<table>
<thead>
<tr>
<th>Interval (min)</th>
<th>Tg (°C)</th>
<th>Tc (°C)</th>
<th>Tm1 (°C)</th>
<th>Tm2 (°C)</th>
<th>ΔHc (J/g)</th>
<th>ΔHm1 (J/g)</th>
<th>ΔHm2 (J/g)</th>
<th>Xc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>55.1</td>
<td>92.9</td>
<td>168.6</td>
<td></td>
<td>32.5</td>
<td>36</td>
<td></td>
<td>38.7</td>
</tr>
<tr>
<td>5</td>
<td>54.3</td>
<td>92</td>
<td>167.6</td>
<td></td>
<td>30.4</td>
<td>41.4</td>
<td></td>
<td>44.5</td>
</tr>
<tr>
<td>10</td>
<td>54</td>
<td>87.3</td>
<td>152</td>
<td>167</td>
<td>3.5</td>
<td>2.5</td>
<td>43.6</td>
<td>49.6</td>
</tr>
<tr>
<td>20</td>
<td>55</td>
<td></td>
<td>152.5</td>
<td>165.8</td>
<td>3.8</td>
<td>40.9</td>
<td></td>
<td>48.1</td>
</tr>
<tr>
<td>30</td>
<td>54.1</td>
<td></td>
<td>152.8</td>
<td>165</td>
<td>5.3</td>
<td>36.3</td>
<td></td>
<td>44.7</td>
</tr>
<tr>
<td>40</td>
<td>52.1</td>
<td></td>
<td>153.1</td>
<td>164.2</td>
<td>54.7</td>
<td></td>
<td></td>
<td>58.8</td>
</tr>
<tr>
<td>50</td>
<td>50.8</td>
<td></td>
<td>153.2</td>
<td>163.1</td>
<td>55.4</td>
<td></td>
<td></td>
<td>59.6</td>
</tr>
<tr>
<td>60</td>
<td>49.1</td>
<td></td>
<td>153.3</td>
<td>162.1</td>
<td>55</td>
<td></td>
<td></td>
<td>59.1</td>
</tr>
</tbody>
</table>

Table 6 illustrates that the enthalpy values increased when the annealing process increases in time. The values were between 36 – 55.4 J/g when the annealing process intervals increased. Therefore, the degree of crystallization was higher as the annealing process increased in length of time, until it became steady at approximately 40 minutes. See Figure 28. The degree of crystallization (%) achieved was 52.5% incrementally, with values ranging from 38% - 60%. The trend exhibited by the degree of crystallization is similar to that found by Angela et al. [92].
3.1.2 Mechanical and Morphological characteristics

A compression test on the PLA samples was performed after undergoing the annealing process. The test was monitored at different periods and the results show how the treatment affects the mechanical properties of these samples.

Figure 29: Degree of crystallization during one hour of annealing processing at 95 °C (Case #2)

Figure 30: Compressive strength $\sigma_u$ and yield strength $\sigma_y$
Figure 30 presents the increase in compressive strength (with a solid fill) and the yield point for the samples as a function of the time taken by the annealing process. Figure 30 shows that compressive strength increased when the annealing period also increased up to a maximum peak of 24-PLA. The increase in annealing processing time increased the strength of the extruded PLA by 84% (from 58 MPa to almost 108 MPa). This behavior is due to an increase in annealing processing time leading to the restful shaping of the spherulites and crystals. This improves compressive strength.
Moreover, Figure 30 shows the yield strength (with pattern fill), which improved as the annealing process time increased up to a maximum of 24-PLA with 104 MPa. As such, it improved by approximately 82%.

Furthermore, compressive modulus E is important for determining mechanical properties. See Figure 31, which shows that compressive modulus E increases with an increase in the time of the annealing process up to a maximum of 24-PLA. The increase in the annealing processing time increased the modulus of extruded PLA by 73% (from 1700 MPa to almost 3000 MPa). This increment corresponds with that of the compressive strength, above. In addition, the reasons why crystals were created as the time taken by the annealing process increased are the very same.

In contrast, Figure 32 illustrates the inverse relation between maximum strain and annealing process times. It shows that the maximum strain decreases as the annealing process times increase resulting in a minimum strain at 24-PLA. Therefore, increasing the annealing processing time reduced the maximum strain on the extruded PLA by 84% (from 0.58 to almost 0.095). The treated PLA samples gradually lose the ability to absorb energy up to the fracture point, when the time of the annealing process is increased.

According to these results, it is clear that the length of the annealing process plays a pivotal role in effecting microstructure level. This was reflected in the test results. The annealing process reduces the degree of molecular randomization and so improves the mechanical modulus and overall strength [81].

In addition, SEM identifies the morphological characteristics of treated PLA. Figure 33 shows the differences between 0-PLA and 24-PLA. The structure is more rigid for 24-PLA than for 0-PLA.
Figure 33: SEM micrograph for PLA specimens at different resolutions

3.2 PLA-DPWP Composites

3.2.1 Thermal conductivity

The thermal conductivity of PLA-DPWP composites was measured at different temperatures from 5 to 50°C. The thermal conductivity coefficients of the PLA-DPWP composites diverse between 0.0693 and 0.0757 $W/(m \cdot K)$ at 25 °C, with DPWP ranging from 0 wt.% to 50 wt.%, respectively.

The minimum thermal conductivity of the PLA-DPWP composites was 0.0693 $W/(m \cdot K)$ for 30-DPWP composite at 25 °C while still exhibiting relatively high mechanical properties. See section 3.2.7 and Figure 34. In addition, thermal
conductivity (k) at 25 °C (298 K) increased slightly for the 40-DPWP and 50-DPWP composites respectively, after reaching a minimum value of 30-DPWP. Moreover, the corresponding values for the thermal conductivity of all the composites were lower than the thermal conductivity for 3-PLA (k = 0.0812 W/(m·K)) at 25 °C (298 K). Thus, the k value of the 30-DPWP composite was 14.66 % lower than for the 3-PLA, while the minimum reduction of the PLA-DPWP composite was 50-DWP at 6.74%.

Figure 34: Thermal conductivity of PLA-DPWP composites at (25 °C)

Figure 35: Thermal conductivity of PLA-DPWP composites at (273 – 323 K)
There are two competing factors that control the thermal conductivity trend shown in Figure 34. These factors are the DPWP content and the number of air voids in the composites. The $k$ value of the DPWP waste was $0.0626 \text{ W/(m}. \text{K)}$, which is relatively lower than the corresponding $k$ value of the 3-PLA. Therefore, the agglomeration of DPWP caused by increasing the DPWP content and reducing air voids led to a slight increase in thermal conductivity where there was a high DPWP content [93, 94]. Air, DPWP and PLA have a different thermal conductivity, and that may explain the slight increase in thermal conductivity. Figure 36 shows a 3D surface model of the $k$ for PLA-DPWP.

Figure 35 demonstrates the thermal conductivity of PLA-DPWP composites at different temperatures from 5 to 50 °C. It shows that, the thermal conductivity
Coefficient of the samples depends on temperature change and is linear in nature. This linear dependency can be expressed by equation (5):

\[ k = C + mT \]  

(5)

where \( k \) is the thermal conductivity coefficient, \( C \) and \( m \) are constants, and \( T \) is the temperature in K.

The remarkably tiny \( m \) values in Table 7 indicate that the thermal conductivity of the PLA-DPWP composite is only marginally dependent on temperature. This is considered a feature for the composite as its thermal conductivity coefficient will not change significantly with temperature in building construction materials. A huge consideration in hot climates.

This composite has low thermal conductivity compared to other composites made from waste wood or expanded polystyrene (0.196-0.274 \( W/(m.K) \)), such as those developed by Agoua et al. [95], or the date palm leaflets and expanded polystyrene waste composites developed for thermal insulation by Masri et al (0.120-0.158 \( W/(m.K) \)) [71]. In addition, this composite allows for the replacement of 50 wt.\% of the PLA, a biodegradable polymer, with a filler derived from natural waste.

Several theoretical and empirical models have been proposed in the literature to predict the thermal conductivity of polymer composites [96-98]. In this work, the simplest approach is followed to model the thermal conductivity data, where it has two limiting cases: linear mixing rule (parallel conduction model, equation (6)) and inverse mixing rule (series conduction model, equation (7)):

\[ k = (1 - \phi)k_p + \phi k_f \]  

(6)
Here, \( k, k_p, \) and \( k_f \) are the thermal conductivity of the composite, PLA and filler (DPWP or DPP), respectively, and \( \phi \) is the volume fraction of filler.

A widely used model to describe the effect of filler particles on the thermal conductivity of a randomly dispersed, particles in a polymer matrix was proposed by Hashin and Shtrikman [99, 100]:

\[
k = \left[ \frac{(1 - \phi)}{k_p} + \frac{\phi}{k_f} \right]^{-1} \tag{7}
\]

Where:

\[
\frac{k}{k_p} = \frac{1 + (d - 1)\phi \beta}{1 - \phi \beta} \tag{8}
\]

\[
\beta = \frac{k_f - k_p}{k_f + (d - 1)k_p} \tag{9}
\]

In the current case, the DPWP particles are assumed to be cylindrical fiber, where \( d \) takes the value of 2 [99]. The validity of the experimental thermal conductivity of PLA-DPWP composites with the above three models is shown in Figure 34. Both the parallel conduction model and the series conduction model were used here to fit the experimental data as the all linear properties values (except 50-DPWP) are bracketed by these two, where series model provides the lower bound and parallel model provides the upper bound [98].

It is clear that the series conduction model provides the best description of the thermal conductivity data of the prepared composites. In the series model, which is a lower bound equation, it is reasonably relevant for composites where the fillers are distributed in a matrix and there is no percolation also at high filler volume fractions.
Moreover, the series model fits well the experimental thermal conductivity of the prepared composites at low wt. % but start to diverge clearly after 30-DPWP.

<table>
<thead>
<tr>
<th>Content (wt. %)</th>
<th>c ((W/(m \cdot K)))</th>
<th>m ((W/(m \cdot K^2)))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-PLA</td>
<td>0.0743</td>
<td>0.0014</td>
<td>0.9988</td>
</tr>
<tr>
<td>10-DPWP</td>
<td>0.0669</td>
<td>0.0014</td>
<td>0.9996</td>
</tr>
<tr>
<td>20-DPWP</td>
<td>0.0636</td>
<td>0.0012</td>
<td>0.9985</td>
</tr>
<tr>
<td>30-DPWP</td>
<td>0.0629</td>
<td>0.0012</td>
<td>0.9987</td>
</tr>
<tr>
<td>40-DPWP</td>
<td>0.0664</td>
<td>0.0013</td>
<td>0.999</td>
</tr>
<tr>
<td>50-DPWP</td>
<td>0.0697</td>
<td>0.0014</td>
<td>0.9988</td>
</tr>
</tbody>
</table>

In a standard home there are two kinds of wall: interior and the exterior which may be exposed to the sun. Any wall exposed to the sun typically contains insulation. The inside walls are usually made from a concrete medium, plaster sand, and sandstone (if required), and have thermal conductivities of 0.7, 0.71 and 1.7 \(W/(m \cdot K)\), respectively [101], while walls exposed to the sun contain polyester of \(\Delta x = 6\) cm of the concrete medium’s thickness.

Figure 37 shows the components of walls and various new designs. The following calculation will compare these walls and the new designs.

The overall resistance of inside home walls without insulation is calculated to be \(0.356\ m^2 \cdot K/W\), where the thickness of the concrete is 20 cm. See equation (10):
\[ R_{\text{overall}} = \sum_{i=1}^{n} \frac{\Delta x_i}{k_i} \quad (10) \]

Where \( R_{\text{overall}} \) is the overall resistant, \( k_i \) is the thermal conductivity of the component, and \( \Delta x_i \) is the thickness of the component.

Design #1: Typical thickness of the polyester (\( k = 0.05 \text{ W/m.K} \)) is 6 cm of the concrete’s thickness. The overall resistant will be:

\[ R_{\text{overall}} = \sum_{i=1}^{n} \frac{\Delta x_i}{k_i} = \left( \frac{0.02}{0.7} + \frac{0.14}{0.71} + \frac{0.06}{0.05} + \frac{0.02}{0.7} + \frac{0.03}{1.7} \right) = 1.472 \frac{m^2. K}{W} \]

Thus, an overall resistance of \( 1.472 \frac{m^2. K}{W} \), representing an increment of 313.5%.

Design #2: If polyester is replaced by a product made from the 30-DPWP composite, the overall resistance will be:

\[ R_{\text{overall}} = \sum_{i=1}^{n} \frac{\Delta x_i}{k_i} = \left( \frac{0.02}{0.7} + \frac{0.14}{0.71} + \frac{0.06}{0.0693} + \frac{0.02}{0.7} + \frac{0.03}{1.7} \right) = 1.14 \frac{m^2. K}{W} \]

Therefore, using a PLA-DPWP composite leads to an increment in overall resistance of \( 1.14 \frac{m^2. K}{W} \), representing an increment of 220.2%.

Design #3: Since the composites developed have relatively high compression strength, if half of the concrete’s thickness is replaced by a product made from the 30-DPWP composite, the overall resistance will be:

\[ R_{\text{overall}} = \sum_{i=1}^{n} \frac{\Delta x_i}{k_i} = \left( \frac{0.02}{0.7} + \frac{0.1}{0.71} + \frac{0.1}{0.0693} + \frac{0.02}{0.7} + \frac{0.03}{1.7} \right) = 1.66 \frac{m^2K}{W} \]
Thus, using a PLA-DPWP composite leads to a large increment in overall resistance of $1.66 \, m^2 K/W$, representing an increment of 366.3%.

<table>
<thead>
<tr>
<th>Typical wall (inside the home)</th>
<th>Design #1: Typical wall+ polyester (exposure to sun)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plaster</td>
<td>Polyester</td>
</tr>
<tr>
<td>Concrete</td>
<td></td>
</tr>
<tr>
<td>Sandstone</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Design #2: Replace polyester by 50-DPWP</th>
<th>Design #3: 50-DPWP (10 cm) and block (10 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plaster ($\Delta x = 2$ cm), Concrete, Polyester, 30-DPWP and Sandstone ($\Delta x = 3$ cm)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 37: Components of wall

Generally, design #3 is preferable as it is more resistant than traditional designs (Design #1) and uses less concrete. In addition, the 30-DPWP composite has higher compression strength. See section 3.2.7.

The effect of moisture on thermal conductivity was studied with selected submergence samples (3-PLA, 30-DPWP, and 50-DPWP) in distilled water at 25 °C. The readings for two periods (1 and 3 hours) were taken. Figure 38 shows how the thermal conductivity changed with a boost in the moisture content (%), while Figure
39 represents the thermal conductivity increase, as the time submerged in the water increased. The 3-PLA does not contain any hydrophilic fillers that will absorb water [93, 102]. The amount of moisture (%) been absorbed by the 50-DPWP was higher than for the 30-DPWP due to a higher filler content. Moreover, the 50-DPWP’s thermal conductivity (k) was higher than for the 3-PLA after three hours recording a moisture content of 1.9%. After that, the 3-PLA and 30-DPWP were left in the water until they reached 2% moisture content in order to investigate how long it takes to reach the same moisture content as the 50-DPWP reached in 3 hours. See Figure 40. 30-DPWP took 12 hours to reach 2% moisture with a thermal conductivity 0.079 \( W/m.K \), while the 3-PLA reached 0.064 % moisture after 120 hours in the water after which the test was terminated.

Figure 38: Thermal conductivity at different moisture (%) content of fixed period (3 hours)
3.2.2 Thermal diffusivity ($\alpha$)

Thermal diffusivity calculates the rate of transfer of heat in any material from the hotter extremity to the cooler end. It is basically thermal conductivity divided by density and specific heat capacity. Assuming we have samples devoid of any reaction,
evaporation or relaxation processes, then reversing heat capacity equals the specific heat capacity.

Table 8 shows the thermal diffusivity of the composites developed here. DPWP reduced the thermal diffusivity of the composites as its content increased. The value for 3-PLA was 0.0589 \( mm^2/s \). In general, the thermal diffusivity for the PLA-DPWP composites was lower than for the 3-PLA alone as shown in Figure 41. The lowest value was 0.0429 \( mm^2/s \) at 50-DPWP, which means a 21.8% reduction from 3-PLA. In addition, Figure 42 combines thermal conductivity, thermal diffusivity and specific heat capacity \( C_p \). Overall, DPWP enhances insulation and increases the time required for heat diffusion to occur.

Table 8: Thermal diffusivity \( \alpha \) of PLA-DPWP

<table>
<thead>
<tr>
<th>Content (wt.%)</th>
<th>( k )</th>
<th>( C_p )</th>
<th>( \rho )</th>
<th>PLA-DPWP ( \alpha ) (( mm^2/s ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-PLA</td>
<td>0.0812</td>
<td>1208.44</td>
<td>1224.59</td>
<td>0.05485</td>
</tr>
<tr>
<td>10-DPWP</td>
<td>0.0737</td>
<td>1291.93</td>
<td>1219.87</td>
<td>0.0468</td>
</tr>
<tr>
<td>20-DPWP</td>
<td>0.0697</td>
<td>1288.4</td>
<td>1216.05</td>
<td>0.0445</td>
</tr>
<tr>
<td>30-DPWP</td>
<td>0.0693</td>
<td>1329.36</td>
<td>1193.86</td>
<td>0.0436</td>
</tr>
<tr>
<td>40-DPWP</td>
<td>0.0727</td>
<td>1370.17</td>
<td>1178.13</td>
<td>0.0451</td>
</tr>
<tr>
<td>50-DPWP</td>
<td>0.0757</td>
<td>1487.00</td>
<td>1187.73</td>
<td>0.0429</td>
</tr>
</tbody>
</table>
3.2.3 Thermal properties via DSC

Differential scanning calorimetry, or DSC, is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample is measured as a function of temperature. The following parameters were studied: glass transition temperature ($T_g$), crystallization temperature ($T_c$), melting
temperature ($T_m$), enthalpy of crystallization ($\Delta H_c$), enthalpy of fusion ($\Delta H_m$), and degree of crystallization ($X_c$). The $T_g$ is the temperature at the onset of glass transition, while $T_c$ and $T_{m1}$ were reported at the maximum peak.

From this DSC analysis, the $T_g$ for 3-PLA was 56.28 °C. The addition of DPWP reduced the $T_g$ value from 49 to 54 °C in the first instance. Since, the samples were annealed for three hours during the cooling cycle, the crystallization peak disappeared from the second heating cycle. Therefore, the $T_m$ did not change significantly, and was within a range of 165 to 170 °C, as shown in Figure 43.

In addition, the enthalpy of fusion ($\Delta H_m$) for 3-PLA was 50.3 J/g, and the addition of 10-DPWP increased the enthalpy to 54.6 J/g. This indicates that a natural filler acts as a nucleation agent at that wt. % [103]. After that, the enthalpy decreased dramatically to 30 J/g at 50-DPWP content. These enthalpies were used to calculate the degree of crystallization in equation (4).

The effect of changing the proportion of DPWP on crystallization was clear. At a 10-DWP content, the degree of crystallization (%) increased to 58.7% from 54% (3-PLA). This indicates that DPWP acts as a nucleation agent at that wt. % [103]. After that, the degree of crystallization (%) decreased rapidly to 33% at 50-DWP, as shown in Table 9.

A different approach (ASTM) was used to observe how the DPWP effects its composites. Of the selected composites, the $T_g$ for the extruded PLA was 54.76 °C and its composites decreased to a range of approximately 49 to 53 °C. In contrast, in the first case, the samples were not exposed to an annealing process during the cooling cycle, so the crystallization peak appeared in the second heating cycle. Therefore, the $T_c$ for extruded PLA was 100 °C, and it decreased to a range of 91 to 88 °C as the
DPWP content increased. The enthalpy ($\Delta H_c$) was between 37 and 2 J/g. Moreover, the $T_m$ decreased sharply at 10 wt.% content DPWP to 163 °C from 167 °C for the extruded PLA. Afterwards, it increased slightly to 165 °C at 50 wt.% content DPWP, as shown in Figure 44. In addition, the enthalpy reduced slightly from 45 J/g for the extruded PLA to 43 J/g for 10 wt.% content DPWP. After that, it declined to 28 J/g. These enthalpies were used to calculate the degree of crystallization in equation (4).

![Figure 43: DSC results for PLA-DPWP (Case #1)](image)

**Table 9: DSC results for PLA-DPWP composites (Case #1)**

<table>
<thead>
<tr>
<th>DWP Content (wt. %)</th>
<th>Tg (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-PLA</td>
<td>56.4</td>
<td>168.5</td>
<td>50.3</td>
<td>54.1</td>
</tr>
<tr>
<td>10-DPWP</td>
<td>50</td>
<td>165</td>
<td>54.6</td>
<td>58.7</td>
</tr>
<tr>
<td>20-DPWP</td>
<td>54.2</td>
<td>169.9</td>
<td>44.7</td>
<td>48.1</td>
</tr>
<tr>
<td>30-DPWP</td>
<td>52.3</td>
<td>168.8</td>
<td>43.1</td>
<td>46.3</td>
</tr>
<tr>
<td>40-DPWP</td>
<td>51.6</td>
<td>170.2</td>
<td>30.9</td>
<td>33.2</td>
</tr>
<tr>
<td>50-DPWP</td>
<td>50.8</td>
<td>168.6</td>
<td>30.4</td>
<td>32.7</td>
</tr>
</tbody>
</table>
Moreover, the effect of changing the proportion of DPWP on the degree of crystallization was negative. The degrees of crystallization (%) were 48.6%, 46.3%, 40.2% and 30.4% respectively for the extruded PLA at 10 wt. %, 30 wt. % and 50 wt. % content DPWP, as shown in Table 10.

The average specific heat capacity of the PLA-DPWP composites was measured from 20 to 40 °C. The minimum average specific heat capacity of the PLA-DPWP composites was 1288.4 \( J/(kg \cdot K) \) for the 20-DPWP composite, as shown Figure 42. In addition, the specific heat capacity \( (C_p) \) increasing slightly in the 50-DPWP composites after reaching their minimum value at 20-DPWP. Moreover, the corresponding heat capacity values for all the composites were greater than the heat capacity of pure PLA \( (C_p = 1208 \ J/(kg \cdot K)) \). In fact, the \( C_p \) value of the 20-DWP composite was 6.7% higher than that for the pure PLA, while the highest value for the PLA-DPWP composites was at 50-DPWP at 23.1%.

![Figure 44: DSC results for PLA-DPWP (Case #2)](image-url)
Table 10: DSC results for PLA-DPWP composites (Case #2)

<table>
<thead>
<tr>
<th>DWP Content (wt. %)</th>
<th>Tg (°C)</th>
<th>Tc (°C)</th>
<th>Tm (°C)</th>
<th>(\Delta H_c) (J/g)</th>
<th>(\Delta H_m) (J/g)</th>
<th>Xc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>54.76</td>
<td>99.9</td>
<td>167.3</td>
<td>36.9</td>
<td>45.2</td>
<td>48.6</td>
</tr>
<tr>
<td>10</td>
<td>49</td>
<td>89.5</td>
<td>163.8</td>
<td>20</td>
<td>43</td>
<td>46.2</td>
</tr>
<tr>
<td>30</td>
<td>53.3</td>
<td>91.4</td>
<td>165.3</td>
<td>12</td>
<td>37.3</td>
<td>40.1</td>
</tr>
<tr>
<td>50</td>
<td>51</td>
<td>88</td>
<td>164.8</td>
<td>2.2</td>
<td>28.3</td>
<td>30.4</td>
</tr>
</tbody>
</table>

3.2.4 Density

The experimental and theoretical density of the PLA-DPWP composites are shown in Figure 45. The experimental density was calculated by dividing the prepared sample weight by the measured volume. The densities of the 3-PLA and DPWP were founded to be 1225 and 518 kg/m³, respectively. The density of the 3-PLA is very close to that in the technical data sheet [104]. Also the density of the DPWP is within a range widely reported in recent literature [105]. The experimental outcomes show that the density decreased slightly as the DPWP increased.

The theoretical density was calculated in equation (1). The densities of dry PLA and DPWP were found and used in equation (1). As shown in Figure 45, the theoretical density decreased in a linear fashion with an increase in DPWP content, thanks to the lower density of DPWP. Although the experimental density decreased when filler content was increased, the mixing rule was not valid for this composite where the decrease was very slight. This can be attributed to the different processes that the composites had passed through. Also, if filler is exposed to very high
temperatures that can affect its structure. The percentage error was 11% for 10-DPWP content, and 39% for 50-DPWP content. That can be attributed to several factors, such as the huge difference in size, and the high temperature used in the extruder. Thus, the samples could be volatile and effected by moisture and the degradation of the structure of the natural filler [106]. This could result in a change in density.

In addition, the composite densities were high compared to other thermal insulator composites such as polyester and tire (700 – 1200 kg/m³) [94]. They were also very high compared with the thermal insulations materials listed in a recently published paper [105].

![Figure 45: PLA-DPWP composite density for different filler content](image)

3.2.5 Water Retention

Figure 46 represents water retention for different samples at 25 °C and in hot water at 50 °C. For the first 24 hour, the water retention for the 10-DPWP, 20-DPWP, 30-DPWP, 40-DPWP, and 50-DPWP composites were 0.107%, 0.361%, 0.474%,
0.670%, and 1.201%, respectively. It was obvious that the WR% increased when the DPWP content increased. Figure 47 shows the WR% for DPWP composites over 4,500 hours. Also, Figure 49 shows that cracks started to appear in the samples after the first week. In general, the WR% starts to reach an equilibrium after approximately 2,000 hours at 25 °C.

Figure 46: Water retention of PLA-DPWP composites (After 24 hours)

At 50 °C, every composites’ WR% increased for the first 24 hours, as shown in Figure 46. The highest WR% for the PLA-DPWP composites was 2.8% for the 50-DPWP. After the first week, samples started to crack, especially the 50-DPWP, as shown in Figure 49. This may be attributed to the hydrophilicity of DPWP due to the hydroxyl groups which creates voids due to poor compatibility between the DPWP filler and the polymer matrix [93, 102]. See section 3.4. Generally, the water retention in PLA-DPWP is very low, which is a big advantage for thermal insulation materials such as different types of polyurethane (after 24h: 1% – 6%) [107]. These include building blocks reinforced with mineral wool and sisal (after immersion 24h: 10% -
18%) [108], other natural composites like starch/PLA composites [109], and modified mud brick building materials [110].

Tajvidi and Azad [111] proposed an empirical equation with two parameters for describing the dependence of water absorption on time: \( WR(t) = f(t) \) dependence, as follows:

\[
WR(t) = a(1 - \exp(-bt)) \tag{11}
\]

Where \( WR(t) \) is the water absorption (in percent), \( a \) and \( b \) are constants that are determined by the curve fitting procedure and \( t \) is the time in hours. Further analysis revealed that this two-parameter equation (11) adequately fit our experimental data. From equation (11), it is clear that \( \lim_{t \to \infty} WR(t) = a = WR_{eq} \).

The values of \( WR_{eq} \) and the parameters \( a \) and \( b \) for composites were obtained from the fitting of experimental data with equation (11) using OriginPro 8 software. The fitting parameters obtained for composites are listed in following Table 11. Figure 47 and Figure 48 show that equation (11) fitted well with the water retention data of composite with \( R^2 \) values varied between 0.983 and 0.994 for cold water while 0.944 and 0.9885 of hot water.
Figure 47: Water retention of PLA-DPWP composites (25 °C, long term)

Figure 48: Water retention of PLA-DPWP composites (50 °C, short term)
Figure 49: Water retention (%) samples at different times

Table 11: Water absorption parameters for PLA-DPWP at cold water and hot water

<table>
<thead>
<tr>
<th>DPWP (wt.%)</th>
<th>Cold water (DPWP)</th>
<th>Hot water (DPWP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>10</td>
<td>6.317</td>
<td>3.61E-04</td>
</tr>
<tr>
<td>20</td>
<td>5.056</td>
<td>0.0015</td>
</tr>
<tr>
<td>30</td>
<td>8.123</td>
<td>0.0017</td>
</tr>
<tr>
<td>40</td>
<td>8.690</td>
<td>0.0016</td>
</tr>
<tr>
<td>50</td>
<td>10.220</td>
<td>0.0023</td>
</tr>
</tbody>
</table>
3.2.6 Chemical Resistant

Figure 50 illustrates variation in the citric acid impregnation capacity of composite specimens, as a function of their filler content. It is clear that increasing filler content increases citric acid absorption up to a maximum of 1.46% at a filler content of 50-DPWP, on the first day. Solution retention values for all the composites ranged between 0.1% and 1.46%. The acidic medium did not have an impact on the body of the samples, see Figure 51 and Figure 52. It should be mentioned that the percentage of citric acid absorption is comparable with that of the water retention test. Moreover, the increase in citric acid absorption by DPWP content may be due to a poor interface between the DPWP particles and the PLA matrix, evident in the SEM images of the composites (see next section).

![Figure 50: Effect of citric acid impregnation on the composites with changing DPWP content (after 24 hours)](image)

Figure 53 shows the sodium hydroxide (NaOH) impregnation capacity of the composite specimens, as a function of filler content. The composites show a negative absorption percentage, which means that the NaOH dissolves parts of the composite.
After the first day, \( \text{NaOH} \) impregnation attains saturation at a filler loading greater than 10 weight percentages. That means increasing the filler loading to a minimum of 10\% to increase the alkaline resistance of the composites.

![Graph showing citric acid impregnation effect on composites](image)

**Figure 51:** Effect of citric acid impregnation on the composites with changing DPWP content (24 hours)

![Image of PLA-DPWP samples](image)

**Figure 52:** PLA-DPWP samples after one week

The reduction in wt. \% was very large as it reached nearly 90\% of all composites. In addition, the alkaline medium had an enormous impact on the composites as the
samples disappeared within a day and half, as shown in Figure 54 and Figure 55. Also, pure PLA was affected by the alkalinity but only slowly, reaching to negative 20% after a week. See Figure 54.

Figure 53: Effect of NaOH impregnation on the composites with changing DPWP content (after 24 hours)

Figure 54: Effect of NaOH impregnation on the composites with changing DPWP content (one week)
3.2.7 Compression Test

PLA-DPWP composites were prepared with contents of DPWP 0 to 50 wt.% and exposed to compression. The stress-strain behavior of the DWP-PLA composites is shown in Figure 56. The test results are summarized in Table 12.

The samples were held between two moveable flat plates in order to compress them at an overhead speed of 1.3 mm/ min. The mean compression yield strength of the 3-PLA was found to be 96.3 MPa.

The yielding strain values for all the composites were between 0.1 - 0.073. These findings illustrate the brittle behavior of the PLA-DPWP composites. Therefore, increasing the DPWP content leads to a corresponding reduction in the break elongation of the composites relative to 3-PLA. This can be attributed to the inherent
rigidity of the DPWP particles, leading to a loss in ductility in the composites. Table 12 shows how the composites with increased DPWP content become gradually less plastic and more resistant to deformation than the 3-PLA. This is reflected in the increased modulus once the DPWP content has been increased. See Figure 57.

![Stress-strain curve for DWP-PLA composites](image)

**Figure 56: Stress-strain curve for DWP-PLA composites**

<table>
<thead>
<tr>
<th>Content (wt. %)</th>
<th>Mean Modulus $E$ (GPa)</th>
<th>Mean Strength $\sigma_u$ (MPa)</th>
<th>Yield Point $\sigma_y$ (MPa)</th>
<th>Strain (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-PLA</td>
<td>2.818±0.213</td>
<td>96.35±8.5</td>
<td>92.79±2.31</td>
<td>0.10±0.008</td>
</tr>
<tr>
<td>10-DPWP</td>
<td>2.759±0.033</td>
<td>79.54±5.45</td>
<td>79.09±4.7</td>
<td>0.10±0.03</td>
</tr>
<tr>
<td>20-DPWP</td>
<td>2.397±0.628</td>
<td>53.08±3.84</td>
<td>52.97±3.75</td>
<td>0.09±0.02</td>
</tr>
<tr>
<td>30-DPWP</td>
<td>2.676±0.236</td>
<td>62.5±4.05</td>
<td>62.5±4.05</td>
<td>0.08±0.008</td>
</tr>
<tr>
<td>40-DPWP</td>
<td>2.666±0.169</td>
<td>64.84±3.55</td>
<td>64.84±3.55</td>
<td>0.08±0.008</td>
</tr>
<tr>
<td>50-DPWP</td>
<td>3.127±0.054</td>
<td>65.53±7.6</td>
<td>64.48±9.39</td>
<td>0.07±0.006</td>
</tr>
</tbody>
</table>

Table 12: Compression properties for PLA-DPWP composites
It can be deduced from Figure 58 that the compression strength of 3-PLA (96.35 MPa) was reduced by 45% to 53 MPa for the 20-DPWP. Afterwards, the strength increased slightly to 65 MPa for the 50-DPWP. SEM imaging can help to explain the reasons for the reduction in strength when added to the DPWP. See Figure 87 and Figure 88. They indicate inhomogeneity at the fracture surface, with voids and DPWP particles noticeable and the rough rims of the voids becoming the consequence of particle pull-out. Moreover, convincing proof of particle pull-out is present with a higher magnification picture. This shows the gaps that occur in the PLA matrix interface with the DPWP particles.

![Figure 57: Yielding strain vs. DPWP content](image)

In the same vein, the compression modulus decreased initially by 15% at 20-DPWP. Afterwards, it increased again until it reached above the value of pure PLA (2.82 GPa) by about 11% at 50-DPWP. This increase indicates that the material produced became progressively less plastic and more resistant to deformation than is the case with PLA as DPWP content increased. This is similar to findings in a paper
published in 2009 [93]. In general, the compression modulus for PLA-DPWP composites was within a range from 2.87 GPa to 2.4 GPa, as shown in Figure 59.

Figure 58: Compression strength vs. DPWP content

Figure 59: Compression modulus vs. DPWP content
The compression strength and modulus are extremely high compared with other thermal insulation materials, e.g. polyester and its composites with tire (strength: 19 -103 MPa and modulus: 264 – 1370 MPa) [112], or soil cement blocks reinforced with mineral wool and sisal (strength: 3 – 4.5 MPa and modulus: 0.02 – 0.7 MPa) [108].

Two potential reasons can explain the drop in the mechanical properties of the composites: poor compatibility between the natural fillers and the matrix, and the agglomeration of the natural fillers. Most especially, the polar surface of the DPWP particles are unlikely to interact strongly with the less polar PLA host matrix. This results in poor compatibility [93, 102]. In addition, the presence of hydrogen bonds may cause the agglomeration of natural fillers, due to the presence of hydrogen bonds in the filler content [113].

In terms of tensile strength, only three composites passed the tensile strength test because of their brittle behavior. Therefore, it was not possible to complete the test. The 3-PLA samples showed tensile strength of 13.4 MPa, a modulus of 46.5 MPa and strain of 5.6. 10-DPWP recorded a tensile strength of 16.3 MPa, a modulus of 14.9 MPa and a strain of 1.2, while the 20-DPWP had a tensile strength of 12 MPa, a modulus of 2.2 MPa and a strain of 0.3.

3.3 PLA-DPP Composites:

3.3.1 Thermal conductivity

The thermal conductivity of the PLA-DPP composites was measured at different temperatures from 5 to 50 °C. The thermal conductivity coefficients at 25°C for the PLA-DPP composites diverse from 0.0712 to 0.0794 W/(m .K), with DPP contents ranging from 0 wt. % to 40 wt. %, respectively.
At 25 °C (298 K), the thermal conductivity (k) for all the composites were lower than the thermal conductivity of 3-PLA. In general, thermal conductivity was reduced slightly in the first three composites with a 3.5% reduction followed by a clear decrease in the 40-PLA composite. The lowest value for thermal conductivity was 0.0712 W/(m .K) at 40-DPP with a 13% reduction compared to the 3-PLA. See Figure 60.

Figure 60: Thermal conductivity of PLA-DPP composites at (25 °C)

Figure 61: Thermal conductivity of PLA-DPP composites at (273 – 323 K)
Figure 62: 3D surface model showing dependence of thermal conductivity on temperature of PLA-DPP

Similar to DPWP, there are two main factors contributing to the thermal conductivity trends observed and shown in Figure 60. These factors are the content of the DPP and the number of air voids in the composites. The k value of the DPP waste was 0.063 \( W/(m \cdot K) \), which is lower than that of the PLA. Therefore, an even distribution of DPP by increasing DPP content and reducing air voids leads to less thermal conductivity at a high DPP content [94]. The differences in the thermal conductivity of air, DPP and PLA may explain the slight increase in thermal conductivity.

Figure 61 demonstrates the thermal conductivity of PLA-DPP composites at different temperatures from 5 to 50 °C. This demonstrates that the thermal conductivity
coefficient of the samples correlates in a linear fashion with changes in temperature. This linear dependency can be expressed by equation (5).

The remarkably tiny $m$ values in Table 13 indicate that the thermal conductivity of the PLA-DPP composite is only marginally dependent on temperature. This is a feature, as the thermal conductivity coefficient is not going to alter drastically due to temperature in building construction materials. This is especially important in hot climate. Figure 62 shows a 3D surface model of the thermal conductivity of the PLA-DPP.

This composite has low thermal conductivity when compared to other composites made of waste wood and expanded polystyrene (0.196 - 0.274 $W/(m \cdot K)$), such as those developed by Agoua et al. [95], or the date palm leaflets and expanded polystyrene waste composites developed for thermal insulation by Masri et al (0.120-0.158 $W/(m \cdot K)$) [71]. In addition, this composite enables the replacement of 40 wt.% of the PLA, a biodegradable polymer, with a natural filler derived from waste products.

<table>
<thead>
<tr>
<th>Content (wt. %)</th>
<th>$c$ ($W/(m \cdot K)$)</th>
<th>$m$ ($W/(m \cdot K^2)$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-PLA</td>
<td>0.0743</td>
<td>0.0014</td>
<td>0.9988</td>
</tr>
<tr>
<td>10-DPP</td>
<td>0.0718</td>
<td>0.0015</td>
<td>0.9946</td>
</tr>
<tr>
<td>20-DPP</td>
<td>0.0713</td>
<td>0.0014</td>
<td>0.9972</td>
</tr>
<tr>
<td>30-DPP</td>
<td>0.0715</td>
<td>0.0014</td>
<td>0.9993</td>
</tr>
<tr>
<td>40-DPP</td>
<td>0.0645</td>
<td>0.0013</td>
<td>0.9982</td>
</tr>
</tbody>
</table>
Similarly of the PLA-DPWP linear mixing rule (parallel conduction model, equation (6)), inverse mixing rule (series conduction model, equation (7)) and Hashin and Shtrikman were followed to model the thermal conductivity data.

In the current case, the DPP particles are assumed to be spherical, where d takes the value of 3 [100, 114]. The validity of the experimental thermal conductivity of PLA-DPP composites with the above three models is shown in Figure 60. Series model provides the lower bound and parallel model provides the upper bound [98].

It is clear that both the parallel conduction model and Hashin and Shtrikman model provide the closest description of the thermal conductivity data of the prepared composites. In the parallel model, which is an upper bound equation, the DPP and PLA matrix contribute independently to the composite thermal conductivity, in proportion to their relative volume fraction. Furthermore, the parallel model fits well the experimental thermal conductivity of the prepared composites (except 30-DPP).

Figure 63 shows the components of walls and new designs. The following calculation compares the walls with the new designs. The overall resistance of an inside home wall without insulation is calculated as $0.356 \, m^2.K/W$ with a typical concrete thickness of 20 cm using equation (10).

Design #1: Typical thickness of the polyester ($k = 0.05 \, W/m.K$) is 6 cm of the concrete’s thickness. The overall resistant will be:

\[
R_{\text{overall}} = \sum_{i=1}^{n} \frac{\Delta x_i}{k_i} = \left(\frac{0.02}{0.7} + \frac{0.14}{0.71} + \frac{0.06}{0.05} + \frac{0.02}{0.7} + \frac{0.03}{1.7}\right) = 1.472 \, m^2.K/W
\]

Thus, the overall resistance of $1.472 \, m^2.K/W$, represents an increment of 313.5%.
Design #2: If polyester is replaced by a product made from 40-DPP composite, the overall resistance will be:

\[ R_{overall} = \sum_{i=1}^{n} \frac{\Delta x_i}{k_i} = \left( \frac{0.02}{0.7} + \frac{0.14}{0.71} + \frac{0.06}{0.0712} + \frac{0.02}{0.7} + \frac{0.03}{1.7} \right) = \frac{1.11}{m^2.K/W} \]

Therefore, using a PLA-DPP composite leads to an increase in the overall resistance of the wall of 1.11 \( m^2.K/W \), representing an increase of 211.8%.

Design #3: Since the composites have high compression strength half of the concrete’s thickness can be replaced by a product made from the 40-DPP composite. Thus, the overall resistance will be:
\[ R_{\text{overall}} = \sum_{i=1}^{n} \frac{\Delta x_i}{k_i} = \left( \frac{0.02}{0.7} + \frac{0.1}{0.71} + \frac{0.1}{0.0712} + \frac{0.02}{0.7} + \frac{0.03}{1.7} \right) = 1.62 \frac{m^2 K}{W} \]

Therefore, using a PLA-DPP composite leads to a large increase in the overall resistance of the wall of 1.62 \( m^2 K/W \), giving an increase of 355%.

Design #3 would be the preference as it has more resistance than a traditional design (design #1) and less concrete will be required. Moreover, 40-DPP has a very high compression strength. See section 3.3.7.

The impact of moisture on the thermal conductivity was studied by submerging selected samples (3-PLA, 20-DPP, and 40-DPP) in distilled water at 25 °C. The results or two periods (1 and 3 hours) were noted. Figure 64 shows how the thermal conductivity changed with increased moisture content (%), while Figure 65 represents the increase in thermal conductivity with the increased length of submergence in the water, with the exception of 3-PLA which does not have any hydrophilic fillers that can absorb water [93, 102]. The amount of the moisture (%) absorbed in the 40-DPP was higher than for 20-DPP. After submerging 20-DPP and 40-DPP for an hour, their respective k values, were greater that for 3-PLA. Moreover, after three hours the 20-DPP and 40-DPP samples were damaged as shown in Figure 67.

To investigate how long 3-PLA and 20-DPP takes to reach the same percentage (%) of moisture as 40-DPP reached in 3 hours, they were left in water until they had reached 9% moisture. See Figure 66. The 20-DPP took 12 hours to reach 9% moisture, with a thermal conductivity 0.079 \( W/m. K \), while the 3-PLA reached only 0.064% moisture after 120 hours in water at which point the test was terminated.
Figure 64: Thermal conductivity at different moisture (%) content

Figure 65: Thermal conductivity at different submergence times in distilled water
3.3.2 Thermal diffusivity (α)

Thermal diffusivity indicates the rate of heat transfer in a material from the hotter extremity to the cooler end. It is thermal conductivity divided by density and specific heat capacity. Assuming we have samples without any reaction, evaporation or relaxation processes, then the reversing heat capacity equals the specific heat capacity.
Table 14 shows the thermal diffusivity of the composites developed here. It can be seen that the DPP reduces the thermal diffusivity of the composites as the content increases. The value of the 3-PLA was 0.0589 \( mm^2/s \). In general, the thermal diffusivity of the PLA-DPP composites was lower than for the 3-PLA. See Figure 68. The lowest value was 0.0358 \( mm^2/s \) at 40-DPP, which means a 34.8% reduction as compared to the 3-PLA. In addition, Figure 69 combines thermal conductivity, thermal diffusivity and specific heat capacity (\( C_p \)). Overall, DPP enhances the insulation material and increases the time it needs to diffuse heat.

<table>
<thead>
<tr>
<th>Content (wt. %)</th>
<th>k ( W/(m .K) )</th>
<th>( C_p ) ( J/(kg .K) )</th>
<th>( \rho ) ( kg/m^3 )</th>
<th>PLA-DPP ( \alpha ) (( mm^2/s ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-PLA</td>
<td>0.0812</td>
<td>1208.44</td>
<td>1224.59</td>
<td>0.05485</td>
</tr>
<tr>
<td>10-DPP</td>
<td>0.0794</td>
<td>1383.79</td>
<td>1212.84</td>
<td>0.047315</td>
</tr>
<tr>
<td>20-DPP</td>
<td>0.0782</td>
<td>1459.31</td>
<td>1208.38</td>
<td>0.043303</td>
</tr>
<tr>
<td>30-DPP</td>
<td>0.0786</td>
<td>1595.81</td>
<td>1202.07</td>
<td>0.040987</td>
</tr>
<tr>
<td>40-DPP</td>
<td>0.0712</td>
<td>1652.31</td>
<td>1203.95</td>
<td>0.035789</td>
</tr>
</tbody>
</table>

Figure 68: Thermal diffusivity for the PLA-DPP composites
3.3.3 Thermal properties via DSC

PLA-DPP composites were tested using DSC. The following parameters were reported: glass transition temperature (T\text{g}), crystallization temperature (T\text{c}), melting temperature (T\text{m}), the enthalpy of crystallization (\Delta H\text{c}), the enthalpy of fusion (\Delta H\text{m}), and degree of crystallization (X\text{c}). The T\text{g} was reported as the temperature at the onset of the glass transition, while the T\text{c} and T\text{m} were reported at the maximum peak.

Figure 70 shows the first analysis and shows that the T\text{g} has decreased slightly with an increase in the DPP filler up to 30 wt.%. It then increased slightly up to 40-DPP, as shown in Another study was conducted according to ASTM standards for a selected proportion of the DPP. As with case #2 in the previous PLA-DPWP composite experiments, there was no annealing process, thus the crystallization peak appeared as shown in Figure 71. The T\text{g} reading was steady with at 54 °C, and the crystallization temperature (T\text{c}) for pure PLA was 100 °C. Adding DPP reduced the T\text{c} up to 93 °C at the 40 wt. DPP content, with an enthalpy that was reduced from 37 J/g to 15 J/g. Moreover, the melting temperature (T\text{m}) was slightly reduced.
In Table 16, the enthalpy of fusion ($\Delta H_m$) increased marginally at 10 wt.% DPP content. Afterwards, the enthalpy decreased sharply at higher contents of 40 wt.% DPP. Furthermore, the degree of crystallization was then calculated in equation (4). The effect of changing the DPP content on the degree of crystallization had a negative effect as in case #2 with the PLA-DPWP content.

Table 15. Similar to the PLA-DPWP composites, these samples were annealed for three hours during the cooling cycle, so the crystallization peak disappeared from the second heating cycle. Moreover, the melting temperature ($T_m$) reduced slightly.

Another study was conducted according to ASTM standards for a selected proportion of the DPP. As with case #2 in the previous PLA-DPWP composite experiments, there was no annealing process, thus the crystallization peak appeared as shown in Figure 71. The Tg reading was steady with at 54 °C, and the crystallization temperature ($T_c$) for pure PLA was 100 °C. Adding DPP reduced the $T_c$ up to 93 °C at the 40 wt. DPP content, with an enthalpy that was reduced from 37 J/g to 15 J/g. Moreover, the melting temperature ($T_m$) was slightly reduced.

In Table 16, the enthalpy of fusion ($\Delta H_m$) increased marginally at 10 wt.% DPP content. Afterwards, the enthalpy decreased sharply at higher contents of 40 wt.% DPP. Furthermore, the degree of crystallization was then calculated in equation (4). The effect of changing the DPP content on the degree of crystallization had a negative effect as in case #2 with the PLA-DPWP content.

Table 15 shows the enthalpy of fusion ($\Delta H_m$) increasing slightly at a 10-DPP content. Afterwards, the enthalpy decreased sharply at higher contents such as 30-DPP and 40-DPP. Furthermore, the degree of crystallization (%) was calculated in equation
(4), where the effect of changing the DPP content on the degree of crystallization was clear. At 10-DPP, the degree of crystallization was steady at approximately 54%, which indicates that the natural filler acted as a nucleation agent at that wt. % [103]. After that, the degree of crystallization decreased slightly at 20-DPP content, and then more rapidly until reaching 37% at a 40-DPP content. The degree of crystallization in the second case followed the same pattern as the first case. In general, the values for the degree of crystallization in the first case were larger than in second case for both fillers and is attributed to the cooling time in the first cooling cycle.

![Figure 70: DSC results for PLA-DPP (Case #1)](image)

Another study was conducted according to ASTM standards for a selected proportion of the DPP. As with case #2 in the previous PLA-DPWP composite experiments, there was no annealing process, thus the crystallization peak appeared as shown in Figure 71. The Tg reading was steady with at 54 °C, and the crystallization temperature (Tc) for pure PLA was 100 °C. Adding DPP reduced the Tc up to 93 °C.
at the 40 wt. DPP content, with an enthalpy that was reduced from 37 J/g to 15 J/g. Moreover, the melting temperature (Tm) was slightly reduced.

In Table 16, the enthalpy of fusion ($\Delta H_m$) increased marginally at 10 wt.% DPP content. Afterwards, the enthalpy decreased sharply at higher contents of 40 wt.% DPP. Furthermore, the degree of crystallization was then calculated in equation (4). The effect of changing the DPP content on the degree of crystallization had a negative effect as in case #2 with the PLA-DPWP content.

Table 15: DSC results for PLA-DPP composites (Case #1)

<table>
<thead>
<tr>
<th>DPP Content (wt. %)</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>Xc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>56.4</td>
<td>168.5</td>
<td>50.3</td>
<td>54.1</td>
</tr>
<tr>
<td>10</td>
<td>52.9</td>
<td>166.2</td>
<td>50.6</td>
<td>54.4</td>
</tr>
<tr>
<td>20</td>
<td>52.9</td>
<td>169</td>
<td>39.32</td>
<td>42.3</td>
</tr>
<tr>
<td>30</td>
<td>51</td>
<td>167.6</td>
<td>38.23</td>
<td>41.1</td>
</tr>
<tr>
<td>40</td>
<td>54.6</td>
<td>167</td>
<td>34.9</td>
<td>37.5</td>
</tr>
</tbody>
</table>
Table 16: DSC results for DPP-PLA composites (Case #2)

<table>
<thead>
<tr>
<th>DWP Content (wt. %)</th>
<th>Tg (°C)</th>
<th>Tc (°C)</th>
<th>Tm (°C)</th>
<th>ΔHc (J/g)</th>
<th>ΔHm (J/g)</th>
<th>Xc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>54.76</td>
<td>99.9</td>
<td>167.3</td>
<td>36.9</td>
<td>45.2</td>
<td>48.6</td>
</tr>
<tr>
<td>10</td>
<td>53.8</td>
<td>96.74</td>
<td>166.2</td>
<td>28.5</td>
<td>45.9</td>
<td>49.4</td>
</tr>
<tr>
<td>30</td>
<td>53.75</td>
<td>94.75</td>
<td>165.1</td>
<td>18.6</td>
<td>38</td>
<td>40.9</td>
</tr>
<tr>
<td>40</td>
<td>53.6</td>
<td>93.3</td>
<td>166</td>
<td>14.86</td>
<td>34.9</td>
<td>37.5</td>
</tr>
</tbody>
</table>

The average reversing heat capacity for the PLA-DPP composites was measured over range from 20 to 40 °C. The average reversing heat capacity for the PLA-DPP composites varied from 1208.4 and 1652.3 $J/(kg\cdot K)$, with the DPP content ranging from 0 wt. % to 40 wt. %, respectively.

The specific heat capacity ($C_p$) for all the composites was higher than the pure PLA. The lowest value for specific heat capacity was 1383.8 $J/(kg\cdot K)$ at 10 wt. %
DPP content, followed by, 20-DPP content at 1,459.3 \(J/(kg \cdot K)\). The two respective wt. % DPP contents increased their specific heat capacity compared to pure PLA by 14.5% and 20.8%, respectively. In addition, the \(C_P\) values increased up to a maximum at 40-DPP, which was 1652.3 \(J/(kg \cdot K)\), as shown in Figure 69.

### 3.3.4 Density

The experimental and theoretical density of the PLA-DPP composites are shown in Figure 72. The experimental density is found by dividing the prepared sample weight by the measured volume. The densities of the 3-PLA and DPP were found to be 1225 and 768 \(kg/m^3\), respectively. The density of the 3-PLA is very close to that shown in the technical data sheet [104]. The densities of the PLA and DPP were measured by experimentation and used for theoretical calculations. The results show that the density decreased marginally as the DPP increased.

As for the DPWP, the theoretical density was calculated by using equation (1). The densities of the pure PLA and the DPP were calculated in equation (1). Figure 72 shows that theoretical density decreased in a linear fashion as DPP content increased. This is due to the lower density of DPP. Although the experimental density decreased when filler content increased, the mixing rule was not valid for this composite as the decrease was very slight. This can be attributed to the different processes that the composites passed through. Also, the filler was exposed to very high temperatures which could affect its structure. The percentage error was 1.1% for the 10-DPP content and 3.7% for the 40-DPP content. In addition, the densities were high compared to other thermal insulation composites like polyester with tire (700 – 1200 \(kg/m^3\)) [94], and very high compared to the thermal insulations materials listed in a recently published paper [105].
3.3.5 Water retention

The water retention of the PLA-DPP composites is shown in Figure 73. The test was conducted in two different environments: in the first test, samples were immersed in water at a laboratory temperature of 25 °C. In the second test, the water temperature was 50 °C. During the two tests, it was observed that water retention increased with increased filler content. The water retention values for the hot water test were higher than the cold water test values. In the cold water (25 °C) tests, for the first 24 hours the water retention values were less than 2% for all the composites, except the 40-DPP which was 5.6%. Figure 74 shows the WR% for the DPP composites over a 1,400 hour period. Moreover, Figure 76 shows that the samples started to crack after the first week except for the 40-DPP content sample that crumbled at approximately 850 hours. In general, the WR% starts to become steady after approximately 600 hours at laboratory temperatures.
At 50 °C, every composites’ WR% increased for the first 24 hours, as shown in Figure 73. They were all less than 2.2% except for the 40-DPP, which showed approximately 7.2%. After the first week, the samples started to crack, especially the 40-DPP composite. See Figure 76. DPP has a strong polar character which could be the reason for an increased WR% [93, 102]. In addition, polarity creates voids that are induced by poor compatibility between the DPP filler and the polymer matrix [93, 102]. See section 3.4. Although water retention in the PLA-DPP composites was higher than in the PLA-DPWP composites, they were still lower than in other polymeric insulation materials. This include polyester–scrap tire [94], different types of polyurethane (after 24 hours: 1% – 6%) [107], building blocks reinforced with mineral wool and sisal (after immersion for 24 hours: 10% - 18%) [108], other natural composites like starch/PLA composites [109], and modified mud brick used as a building material [105].

The values of $WR_{eq}$ and the parameters (a and b) for composites were obtained from the fitting of experimental data with equation (11) using OriginPro 8 software.

Figure 73: Water retention of PLA-DPP composites (After 24 hours)
The fitting parameters obtained for composites are listed in following Table 17. Figure 74 and Figure 75 show that equation (11) fitted well with the water retention data of composite with $R^2$ values varied between 0.9958 and 0.9973 for cold water while 0.9018 and 0.964 of hot water.

Figure 74: Water retention of PLA-DPP composites (25 °C, long term)
Figure 75: Water retention of PLA-DPP composites (50, short term)

Figure 76: WR% samples at different times

A) 25 °C after one week, B) 50 °C after one week, C) 25 °C after 250 hrs. D) 25 °C after 850 hrs.
Table 17: Water absorption parameters for PLA-DPP at cold water and hot water

<table>
<thead>
<tr>
<th>DPP (wt.%)</th>
<th>Cold water (DPWP)</th>
<th>Hot water (DPP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>10</td>
<td>8.7704</td>
<td>8.50E-04</td>
</tr>
<tr>
<td>20</td>
<td>17.4393</td>
<td>0.0028</td>
</tr>
<tr>
<td>30</td>
<td>18.6834</td>
<td>0.0034</td>
</tr>
<tr>
<td>40</td>
<td>25.3859</td>
<td>0.0104</td>
</tr>
</tbody>
</table>

### 3.3.6 Chemical Resistant

Figure 77 represents variation in the citric acid impregnation capacity of composite samples, as a function of filler content. It is clear that increasing the filler content by more than 10 wt.% sharply increases citric acid absorption. The wt.% of 20-DPP, 30-DPP and 40-DPP were between 1.5% - 1.6% for the first 24 hours. The acidic medium did not have any impact on the samples shown in Figure 78 and Figure 79. The percentage of citric acid absorption was comparable with that of water with less that 30-DPP. Furthermore, increasing citric acid absorption with increasing DPP content may be due to the poor interface between DPP particles and the PLA matrix. This is obvious in SEM images of the composites.
Figure 77: Effect of citric acid impregnation on composites with changing DPP content (after 24 hours)

Figure 78: Effect of citric acid impregnation on composites with changing DPP content (one week)
Figure 80 shows the sodium hydroxide (NaOH) impregnation capacity of the composite samples, as a function of filler content. The composites showed a negative absorption percentage, which means that the NaOH dissolved parts of the composite. After the first day, it is clear that increasing the filler content increased the reduction in wt.% required to reach a maximum value of 82.3% with 40-DPP. In general, the reduction in wt. % was very noticeable as it was above 40% in all the composites. In addition, the alkaline medium has a huge influence on the composites as they dissolved completely within two days (≈ 50 hours), as shown in Figure 81 and Figure 82. Also, the pure PLA was affected by the alkalinity but only slowly as it reached a negative 20% after a week. See Figure 81.
Figure 80: Effect of NaOH impregnation on composites with changing DPP content (after 24 hours)

Figure 81: Effect of NaOH impregnation on composites with changing DPP content (one week)
According to the literature several factors promote the degradation of PLA. If PLA is exposed to abiotic factors, such as temperature, pH, soil moisture, and UV radiation it will experience degradation leading to irreversible changes in the polymer until which will gradually fail and lose its various properties [115, 116]. One of the mechanisms causing degradation is chemical hydrolysis, which mainly occurs due to main chain scission or side chain scission [117]. The following reaction illustrates the hydrolysis of the ester groups in aliphatic polyesters, such as those in PLA, in the presence of water:

\[-\text{COO} + \text{H}_2\text{O} \rightarrow -\text{COOH} + \text{OH}^-\]

The PLA was exposed to a citric acid medium with a measured pH of 2.06, and a NaOH solution with measured pH of 13.5, which is a strong alkaline medium.
Therefore, the PLA interacts with various environments at different levels of pH. The different mediums’ pH levels affect the rate of hydrolysis in PLA-based materials. In a strong acidic and basic medium, polymer chains are easily degraded as the hydrolysis reactions are catalyzed in the presence of hydronium and hydroxide ions [88, 118]. According to these results, the composites displayed greater resistance to citric acid than to NaOH. This is in line with the published literature [119].

3.3.7 Compression Test

The compression behavior of the PLA-DPP composites is shown in Figure 83. The compression properties decrease progressively as DPP content is increased. Usually, the natural filler reduces the mechanical properties of composites due to differences in polarity [102, 103]. Table 18 gives more details regarding these results.

Figure 83: Stress-strain curve for PLA-DPP composites

Figure 84 shows compression strength as a function of filler content. Pure sample strength was measured as 96.35 MPa. Adding DPP to the PLA matrix slightly reduced the compression strength of the composites. The compression strength for the 10-DPP, 20-DPP, 30-DPP and 40-DPP was 90.52 MPa, 80.01 MPa, 67.83 MPa, and
64.36 MPa, respectively. The reduction of compression strength at 40-DPP content was approximately 33%. Indeed, the compression strengths recorded were much higher than that of any other insulation material (2 MPa to 10 MPa) [120], and was comparable to building materials [121, 122]. This value can be further extended by adding chemical modifiers to improve the adhesive properties operating between the filler and the polymer matrix [93].

Table 18: Compression properties for PLA-DPP composites

<table>
<thead>
<tr>
<th>Content (wt. %)</th>
<th>Mean Modulus $E$ (GPa)</th>
<th>Mean Strength $\sigma_u$ (MPa)</th>
<th>Mean Yield Point $\sigma_y$ (MPa)</th>
<th>Mean Strain (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>2.818±0.213</td>
<td>96.35±8.5</td>
<td>92.79±2.31</td>
<td>0.10±0.008</td>
</tr>
<tr>
<td>10</td>
<td>2.875±0.072</td>
<td>90.52±9.12</td>
<td>90.52±9.21</td>
<td>0.063±0.035</td>
</tr>
<tr>
<td>20</td>
<td>2.724±0.138</td>
<td>80.0080±3.1</td>
<td>80.01±3.1</td>
<td>0.063±0.015</td>
</tr>
<tr>
<td>30</td>
<td>2.448±0.310</td>
<td>67.8270±14.57</td>
<td>67.83±14.56</td>
<td>0.056±0.02</td>
</tr>
<tr>
<td>40</td>
<td>2.324±0.360</td>
<td>64.3563±30.56</td>
<td>64.36±30.56</td>
<td>0.044±0.012</td>
</tr>
</tbody>
</table>

On the other hand, the compression modulus increased to 2.87 GPa at a 10-DPP content, followed by a slight decrease to 17.5% at 40-DPP content. Whereas, the pure sample modulus was 2.82 GPa, the higher modulus values indicated that the composites became less plastic and more resistant to deformation than PLA as DPP content increased. In general, the compression modulus for the PLA-DPP composites was within a range between 2.87 GPa and 2.33 GPa, as shown in Figure 85.
Strain is one compression properties that was studied here. Figure 86 shows that increasing DPP content reduced yielding strain quite dramatically. The reduction was 38.1%, 45.4% and 56.4% at 20-DPP, 30-DPP and 40-DPP content, respectively. This exemplifies the brittle behavior of the PLA-DPP composites.

Additionally, compression strength and the modulus were very high compared with other thermal insulation materials such as polyester and its composites with tire
(strength: 19-103 MPa & modulus: 264 – 1370 MPa) [112]. The strength was still higher than some building insulation materials (2.4 to 3.3 MPa) [120] and soil cement blocks reinforced with mineral wool and sisal (strength: 3 – 4.5 MPa & modulus: 0.02 – 0.7 MPa) [108].

**Figure 86: Yielding strain vs. DPP content**

Generally, the reduction in compression properties observed can be attributed to two factors: poor compatibility between the natural fillers and the matrix; and the agglomeration of the natural fillers. The hydroxyl groups (−OH), in particular, present in natural fillers make them hydrophilic, whereas polymers are hydrophobic [123]. This results in poor compatibility [102]. In addition, because of the presence of hydrogen bonds, the natural fillers may agglomerate [113].

When examining tensile test, there were difficulties in the preparation and testing of the PLA-DPP composites. The 10-DPP content was the only composites that did not fail during the test. Therefore, it was not possible to complete these tests. The 10-DPP samples showed a tensile strength of 10.8 MPa, a modulus of 14.3 MPa and strain of 1.5.
3.4 Microstructure of Composites

The samples developed were imaged to investigate adhesion between the fillers and the matrix by using the samples after the compression tests.

The addition of different fillers to the composites led to a reduction in properties such as strength, WR%, chemical resistance, and thermal conductivity. These reductions can be attributed to the agglomeration of the fillers, the creation of stress concentration points, as well as poor compatibility between the fillers and the polymer matrix. The mechanical properties were those properties most affected by the poor compatibility between the filler and the matrix (see above).

The agglomeration of the natural fillers is due to hydrogen bonds between the particles [112]. The agglomeration of DPWP and DPP fillers at a high level of concentration is clearly shown in Figure 87. Unquestionably, the filler particles are weaker than the polymer matrix, thus the particles obstruct stress transfer and can cause stress concentration. Figure 88 shows the cracks and gaps that were created by the additional particles. This confirms that the particles act as stress concentration points. As a result, a reduction in mechanical strength was observed. However, the compression properties of the DPWP composites increased after the 30-DPWP point, where the fillers acted as agents of reinforcement, as shown in Figure 58. In addition, it is clear that poor compatibility between the fillers and the PLA matrix caused a reduction in mechanical properties.
Figure 87: SEM of 50-DPWP & 40-DPP
3.5 Fire testing

Figure 90 shows the setup procedure for the fire test. The fire test was used with the 3-PLA, 30-DPWP, 50-DPWP, 20-DPP and 40-DPP. Since the specimens concerned are not fire retardant, the fire only reached as far as the holding clamp, as shown in Figure 89. Thus, UL94 V is not suitable for this polymer or these composites.
In some articles, it has been suggested that the exposure time is reduced to 5 seconds when this test is carried out for academic research [86, 124].

Therefore, to observe how our composites interact with fire, another examination was conducted where the time required to completely burn the sample was measured. Figure 91 shows how long DPWP samples took to burn completely after exposed to blue fire for 10 seconds, while Figure 92 represents the DPP samples. Two things became apparent. That is the time required was shortened as the content was increased, and the burning material dropped after a longer time when the content was increased.

Figure 89: Fire test for 3-PLA, 50-DPWP and 40-DPP
Figure 90: UL94 V setup

Figure 91: DPWP samples burning time

Figure 92: DPP samples burning time
3.6 Comparison between PLA-DPWP and PLA-DPP

One common characteristic shared by entirely the insulating materials used for constructing purposes is their low thermal conductivity (k). It is typically below 0.1 \( W/(m \cdot K) \) [125]. In this study, the composites developed satisfied the criterion, as well as providing biodegradable insulation materials. In addition, the thermal conductivity reported was less than for a number of thermal insulation materials recently examined in the literature [105].

![Figure 93: Thermal conductivity of PLA-DPWP and PLA-DPP](image)

Figure 93 shows that every filler percentage minimized thermal conductivity to a different degree or percentage. We can see that at a low wt. % of fillers, the k values for PLA-DPP were higher than for the PLA-DPWP composites, while with a higher wt. % (\( \geq 40 \) wt. %) the opposite was true. Generally, these composites were acceptable as thermal insulation materials, but the PLA-DPWP composites were preferable at 50 wt.%. The lowest reduction was 6.7% at 50-DPWP, which was better than all the PLA-DPP composites except for 40-DPP.
Water retention (WR%) is an important test designed to examine the composites developed. Figure 94 shows the WR% for every composite in cold (25 °C) and hot (50 °C) water over a 24 hour period. It can be seen that the PLA-DPP composites start absorbing more water at high filler proportions (> 30 wt.%). On the other hand, the PLA-DPWP composites record very good results when all the composites were at less than 2% (except 50-DPWP which was 3%). Based on this, we can conclude that PLA-DPWP composites have good resistance to water absorption compared to the PLA-DPP composites at high filler proportions. Overall, water retention by both the PLA-DPWP and PLA-DPP composites was excellent.

![Figure 94: Effect of DPWP and DPP fillers on water retention](image)

From a mechanical perspective, traditional thermal insulation materials suffer from poor mechanical properties. Figure 95 shows the acceptable negative effect of the DPWP and DPP on the composites. As such, the results display good values when compared to existing thermal insulation materials and many natural composites. However, the poor interface between the fillers that were added and the PLA matrix caused a degradation in mechanical strength.
These composites have the potential to serve as green thermal insulation materials. Therefore, it is proposed that these composites are suitable as insulation material, especially when composites 50-DPWP and 40-DPP are compared with other commercially available thermal insulation materials discussed in the literature [101, 105, 126-128]. Figure 96 is a comparison of 50-DPWP and 40-DPP with other insulation materials in terms of thermal conductivity, while Figure 97 represent a comparison in compression strength.

Figure 95: Effect of DPWP and DPP fillers on compression strength

Figure 96: Thermal conductivity comparison (insulators and building materials)
Figure 97: Mechanical strength comparison (insulators and building materials)
Chapter 4: Conclusion

In this study, waste-based green thermal insulators were developed with different filler contents (0 to 50 wt.%) using date palm wood powder (DPWP) and date pit powder (DPP) as fillers, and poly lactic acid (PLA) as the polymer matrix. The composites were characterized in terms of their thermal, mechanical and physical properties. Furthermore, the microstructure of the composites produced was explored using SEM methodology. From the results of this investigation, we arrived at the following conclusions:

- Annealing processes affect the properties of pure PLA. Increasing the annealing time at a temperature of 95 °C increases thermal conductivity, density, compressive strength and the compressive modulus of pure PLA, but reduces the maximum strain.
- Optimum annealing conditions (95 °C for 3 hours) were employed to produce composites with the optimum thermal conductivity and mechanical strength.
- Date palm waste can be used to manufacture stable and compatible composites with the PLA polymer.
- PLA-DPWP and PLA-DPP composites can serve as green thermal insulation materials due to their low thermal conductivity, thermal diffusivity and water retention, whilst maintaining high compressive strength.
- The optimum filler content for PLA-DPWP and PLA-DPP composites in terms of thermal conductivity were at 30-DPWP and 40-DPP, respectively. The 30-DPWP reduced thermal conductivity by 14.66%,
while the 40-DPP reduced it by 12.3%. The values for thermal conductivity reported are comparable to many commercial insulators and far less that the thermal conductivity of other natural fiber-based composites.

- The water retention of the composites was low. In general, PLA-DPWP composites displayed better values than the PLA-DPP composites.

- After immersion for 24 hours, the uptake value of the PLA-DPWP composites was < 1.5% and 10% at equilibrium, while the water retention of the PLA-DPP composites was < 6% and 20% at equilibrium, except for composites containing 40-DPP, where water uptake reached 25% at equilibrium.

- Although increasing filler content reduced mechanical properties at the highest wt.%., they still displayed an acceptable level of compressive strength and compressive modulus, when compared with traditional insulation materials and other building materials.

- The compressive strengths of the PLA-DPWP composites varied from 53 to 79.5 MPa, while that the compressive strengths of the PLA-DPP composites ranged from 64 to 90.5 MPa.

- The compressive strengths of the composites prepared here are better than most of the typical materials used in construction like concrete and sandstone. Therefore, it is possible to use these composites in construction alongside concrete. Typical concrete compressive strength is $40 \, N/mm^2$, while typical wall thickness is 27 cm (plaster 2 cm, concrete 20 cm, plaster 2 cm, and sandstone 3 cm).
• Replacing 50% of the concrete in a typical wall by 30-DPWP or by 30-DPP composites, will increase the thermal resistance of the wall by 366.3% and 355%, respectively.

Consequently, one could say that PLA-based composites display excellent characteristics in terms of their thermal conductivity, mechanical properties and water retention. Such cheap and abundant natural fillers are potential green thermal insulation materials for both domestic and industrial applications.

Future Work:

• Chemical treatment of the filler particle may produce samples with better adhesion between the filler and PLA.

• A change to the storage conditions and a study of the environmental impact of the degradation of the PLA and PLA composite. The environmental factors include humidity and temperature. In addition, preparation parameters such as temperature and pressure in compression molding should investigated.

• Perform more detailed experiments with PLA composites that have finer interval concentration levels.

• Cost estimation of the production of PLA-DPWP and PLA-DPP composites on a large scale needs to be pursued.
References


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