The effects of bio-based plasticizing agent and plant-based filler on the mechanical and thermal properties of poly(lactic acid) (PLA)

By

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Abstract

The overwhelming majority of the plastics that are currently used in commercial applications are petroleum-based polymers due to their exceptional properties and low cost. However, these polymers are non-degradable and their excessive use is leading to significant increase in global plastic waste. The environmental and health issues associated with petroleum-based polymers has raised the demand for bio-based and biodegradable polymers as an alternative to reduce the negative impacts of synthetic polymers on the environment. Poly(lactic acid) (PLA) is a bio-based, biodegradable, and biocompatible biopolymer which is considered as a promising alternative to petroleum-based polymers. It has great potential for applications in different areas such as food packaging, pharmaceuticals, and medical applications. However, the production cost for PLA is relatively high compared to its petroleum-based counterparts, and it suffers from high brittleness and low flexibility that limit its large-scale commercial applications.

In this work, the effects of hemp hurds as inexpensive bio-based reinforcing filler on the mechanical and thermal properties of PLA biocomposites were investigated so as to determine the potential of the prepared materials to be used in commercial applications. Additionally, the incorporation of epoxidized canola oil (ECO) as a bioplasticizer (*i.e.* is bio-based plasticizer) into both neat PLA and PLA-hemp hurd composites was studied to determine whether the flexibility issues of PLA-based materials could be improved.

For the purpose of this study, two different chemical treatments were performed on the hemp hurds to potentially improve the filler-matrix interaction once it is introduced into PLA matrix. Then neat PLA pellets were melted and compounded with varying amounts of hemp hurd powder and ECO using a twin-screw extruder. The extruded filaments were hot-pressed to obtain dumbbell-shaped samples for mechanical characterization according to international standards.

The prepared specimens were characterized to determine the effect of hemp hurd powder and ECO on the mechanical and thermal properties of PLA.

Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) analysis were carried out to study the effect of chemical treatments on the morphology and structure of the hemp hurd powder. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements were used to evaluate the thermal properties, thermal stability, and crystallinity of the prepared biocomposites. Tensile testing was used to study the mechanical properties of the prepared samples. Plasticizer migration level was also evaluated according to an international standard.

Characterizations showed that the chemical treatments were effective in removing undesirable components from hemp hurds, which resulted in an enhanced filler-matrix interaction once introduced into PLA matrix. The mechanical and thermal properties of the biocomposites formed with treated hemp hurd powder were improved as compared to the biocomposites containing untreated hemp hurd powder. For all of the biocomposites, the incorporation of hemp hurd powder – either treated or untreated – resulted in an increase in tensile modulus and a reduction in tensile strength compared to neat PLA due to the higher stiffness of the hemp hurds.

The incorporation of epoxidized canola oil (ECO) as a bio-based plasticizer into PLA matrix showed significant improvement in the mechanical properties in terms of elongation at break as compared to neat PLA. The plasticizing effect of ECO was most evident in PLA sample containing 7.5 wt % ECO, as the sample showed an impressive 1732% increase in elongation at break compared to neat PLA. In terms of PLA/hemp hurd powder biocomposites plasticized with ECO, only the sample containing 10 wt % ECO showed elongation at break value higher than neat PLA. Nonetheless, all of the plasticized biocomposites containing hemp hurd powder showed

improved flexibility compared to the samples without ECO, however, this improvement was not significant for the samples containing less than 10 wt % ECO. Moreover, none of the plasticized samples showed significant plasticizer migration levels. Considering the promising results regarding the plasticizing effect of ECO on PLA, it is possible to prepare completely bio-based PLA biocomposites that can be used in commercial applications without causing adverse environmental effects.

Preface

Chapter 3 of this thesis has been submitted for publication as “The effects of alkaline and alkaline/peroxide treatments on the mechanical and thermal properties of PLA/hemp hurd powder biocomposites.” I was responsible for data collection, data interpretation, and writing original draft of manuscript. M. Safder assisted with the data collection and contributed to the manuscript edits. M.A.H. Khondoker contributed to the conceptualization and manuscript edits. A. Elias was the supervisory author and was involved with conceptualization, manuscript composition, and manuscript edits. The data collection and analysis in Chapter 4, concluding analysis in Chapter 5, and literature review in Chapter 2 are my original work.

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Nomenclature and abbreviations

Symbols

T_g	Glass transition temperature (°C)
T_m	Melting temperature (°C)
T_{cc}	Cold crystallization temperature (°C)
σ	Tensile strength (MPa)
E	Young's modulus (Tensile modulus) ((MPa)
ε	Elongation at break (%)
M_n	Number average molecular weight
M_w	Weight average molecular weight
2θ	Diffraction angle in XRD analysis
I_{002}	Peak intensity of crystalline plane of cellulose in XRD analysis
I_{am}	Peak intensity of amorphous cellulose in XRD analysis
I_c	Crystallinity index (%) in XRD analysis
ΔH_m	Enthalpy of melting
ΔH_m^0	Enthalpy of melting of pure crystalline material
w	Weight fraction
X_c	Degree of crystallinity (%) in DSC analysis
T_{10}	Temperature at which 10% weight loss has occurred
T_{50}	Temperature at which 50% weight loss has occurred
T_i	Temperature at which the sample mass has decreased by 5%
T_f	Temperature at which the sample mass has decreased by 90%
T_{peak}	Temperature of the peak in DTG thermogram

Abbreviations

3D	3-dimensional
AHH1	Single-cycle alkaline-treated hemp hurd powder
AHH3	Three-cycle alkaline-treated hemp hurd powder
APHH1	Single-cycle alkaline/peroxide-treated hemp hurd powder
APHH3	Three-cycle alkaline/peroxide-treated hemp hurd powder
ATR	Attenuated total reflectance
bio-PE	Bio-polyethylene
bio-PET	Bio-polyethylene terephthalate
DEHP	Bis(2-ethylhexyl) phthalate
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Derivative of thermogravimetry
ECO	Epoxidized canola oil
ECSO	Epoxidized cottonseed oil
EKO	Epoxidized karanja oil
ELO	Epoxidized linseed oil
ESBO	Epoxidized soybean oil
EVO	Epoxidized vegetable oil
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
HSF	Hazelnut shell flour
MA	Maleic anhydride

PBAT	Polybutylene adipate terephthalate
PBS	Polybutylene succinate
PCL	Poly(ε-caprolactone)
PE	Polyethylene
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoate
PLA	Poly(lactic acid)
PP	Polypropylene
PVA	Polyvinyl acetate
PVC	Poly (vinyl chloride)
ROP	Ring opening polymerization
RWF	Recycled wood fiber
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
THC	Tetrahydrocannabinol
UHH	Untreated hemp hurd powder
VO	Vegetable oil
XRD	X-ray diffraction

1. Introduction

This study investigates the effect of bio-based additives on the thermal and mechanical properties of poly(lactic acid) (PLA) in order to develop a completely bio-based and biodegradable material for potential packaging applications. This chapter includes the motivation for this experimental study. Moreover, the overall outline of the thesis and the objectives of this study will be discussed in this chapter.

1.1. Background and motivation

In the modern world, the demand for plastics has been increased extensively to keep up with the needs of each industry. Most of the industries use synthetic polymers such as polyethylene (PE), polypropylene (PP), Polyethylene terephthalate (PET), and epoxy for their needs due to their highly desirable properties (e.g. strength, flexibility, chemical inertness) and low cost [1]. However, most of these polymers are derived from petroleum and with the depletion of fossil fuel reservoirs, there is an uncertainty regarding the future of the petroleum-based polymers. Additionally, synthetic polymers are usually resistant to various kinds of chemicals and biological agents, which means that they do not decompose easily in the environment [2]. For instance, it is estimated that it could take up to 500 years for a plastic bottle to break down [3]. Furthermore, synthetic polymers – which make up almost 80% of the commercial polymers – could pose adverse impacts on human health and environment if not disposed of properly. Some grave consequences of mismanagement in disposing of plastic wastes are shown in **Figure 1.1**.

Figure 1.1. Plastic waste damaging environment and ecosystems (left), plastic waste detrimental effect on wildlife (right). © 2009 U.S. Fish and Wildlife Service, Creative Commons (CC) by 2.0 [4], [5]

To overcome the issues associated with the synthetic polymers, scientists are working toward development of polymers that are bio-based (i.e. polymers produced from natural feedstock), biodegradable (i.e. polymers that can be degraded by means of microorganisms), and at the same time possessing comparable properties and performance of synthetic polymers. In this pursuit, bio-based and biodegradable biopolymers are among the most extensively researched alternatives to the petroleum-based polymers [2]. Poly(lactic acid) (PLA) a promising candidate, is a high-strength, bio-based, and biodegradable biopolymer. This biopolymer is produced by various microorganisms in the fermentation process of the sugars and/or starch, which are extracted from plants or low-value biomass [6]. Moreover, it is reported that production of PLA requires 20% - 50% less energy as compared to the production of petroleum-based polymers [7]. PLA's biodegradability and biocompatibility make it an attractive candidate to be used in different fields including food packaging, pharmaceutical applications, and medical devices [8], [9]. Although advances in the fermentation process have reduced the market price of PLA in recent years, the production cost of PLA is still considered to be relatively higher than its petroleum-based counterparts [6]. Furthermore, PLA's inherent brittleness (which results in limited flexibility and low elongation at break), is another drawback to the use of this material [10]. These drawbacks limit PLA's wider use in packaging applications which require highly flexible materials. Many strategies including reinforcement with fillers, plasticization, copolymerization, and blending with other polymers have been proposed to overcome the aforementioned shortcomings of PLA [10].

The incorporation of low-cost additives into PLA matrix can both lower the production cost and improve the properties (mainly mechanical and thermal) of the final products. In recent years, there has been extensive interest in using natural fibers as bio-based additives to reinforce the PLA matrix. Natural fibers have desirable properties including excellent mechanical properties, low density, and low cost, which make them a promising reinforcing additive [11]. Some studies have reported that the addition of natural fibers to PLA matrix resulted in improvements in the properties of prepared composites over neat PLA. For instance, Lu et al. reported that the addition of bamboo cellulose fibers to PLA can improve the mechanical and physical properties of the prepared biocomposite provided that good fiber-matrix interaction is achieved [12] .

Plasticization is the most commonly used approach to overcome the flexibility issue of biopolymers such as PLA. In this case, a plasticizer – a low molecular weight compound – is added to the polymer matrix to reduce the high brittleness of the polymer while improving the melt-processing of the polymer. Extensive use of phthalate-based plasticizers such as bis(2-ethylhexyl) phthalate (DEHP), which are dominating the plasticizer market, have raised concerns regarding the environmental and health issues, particularly when they migrate out of the matrix polymer or are released into the environment. Therefore, over the past few years, bioplasticizers (*i.e.* bio-based plasticizers) such as epoxidized vegetable oils are receiving great deal of attention due to their biodegradability, biocompatibility, and bio-based nature [13], [14]. Epoxidation is required to improve the compatibility of vegetable oils with polymer matrix [15]. For example, Liu et al.

studied the effect of epoxidized soybean oil (ESBO) on the toughening of PLA matrix using various concentrations of ESBO [10]. In another study, Hosney et al. reviewed the use of epoxidized vegetable oils as bio-based alternative plasticizers to phthalate-based plasticizers for poly (vinyl chloride) (PVC) formulations [16]. Epoxidized canola oil (ECO), another bio-based oil, could also be used as a bioplasticizer in polymers, in particular biopolymers. However, the impact of ECO on the thermal and mechanical properties of PLA has not yet been investigated.

In this work, the effect of addition of hemp hurd powder and ECO as bio-based additives on the thermal and mechanical properties of PLA-based materials are investigated. These additives are selected to: (1) reinforce the PLA matrix and reduce the final product cost, (2) improve the flexibility of PLA and PLA-based composites. To reinforce the matrix and reduce material costs, hemp hurd powder is added to the matrix. It is desirable to add at least 10 % powder to reduce the material costs. However good interactions must be achieved between the filler and the matrix to ensure that the mechanical properties of the material are equal to or better than that of neat PLA. Therefore, surface modification of the hemp hurd powder is required. To improve flexibility, epoxidized canola oil is added. If ECO shows promising plasticizing effect in this study, it could help the economy of Alberta by finding new applications for the canola oil in this province. PLA typically has an elongation at break of less than 10%; the target of this study is to increase the elongation at break value of plasticized PLA samples to above 50%. Throughout the work, various additive concentrations are used in hopes of improving the properties of PLA-based composites, in a way that these materials could potentially be used in industrial applications.

Extrusion and hot-pressing are the main melt-processing techniques used in this study. In the extrusion process, PLA and the additives are mixed to form filaments, which are cut into pellets to prepare the test samples using hot-pressing machine for mechanical and thermal characterization.

1.2. Objectives of study

The overall objectives of this study are to:

1. Achieve good filler-matrix interaction by investigating various chemical surface modification techniques for hemp hurd powder
2. Determine the optimum filler content in PLA matrix that yields the best mechanical and thermal properties
3. Study the effect of ECO, as bio-based plasticizer, on mechanical and thermal properties of PLA-based composites to develop a more flexible material for potential industrial applications

1.3. Organization of the thesis

This thesis is comprised of five chapters. Chapter 2 is a literature review of PLA, PLA reinforced with natural fibers, and bioplasticizers used in biopolymers. Chapter 3 includes the chemical surface modification (alkaline and alkaline/peroxide) techniques employed to reduce the hydrophilicity of hemp hurd powder to improve its miscibility with hydrophobic PLA matrix. Moreover, the mechanical and thermal characterizations of the treated hemp hurd powder and PLA/hemp hurd powder biocomposites are provided in this chapter, which has been submitted to a journal for publication. Chapter 4 deals with the brittleness issue associated with PLA and the prepared PLA/hemp hurd powder biocomposites. In this chapter, epoxidized canola oil (ECO), a bio-based biodegradable plasticizer, is used in preparation of plasticized PLA and PLA/ hemp hurd powder samples to improve the flexibility of these samples. Finally, chapter 5 includes the overall conclusions of this study and the future work that could extend from the current research.

2. Literature review

2.1. Introduction to poly (lactic acid) (PLA)

2.1.1. Biopolymers

The depletion of petroleum resources and environmental issues associated with the petroleum-derived plastics, is driving the demand for bioplastics more than ever. The term “bioplastics” was first coined by *European Bioplastics* and defined as: (1) a plastic material that is produced from biomass such as corn (*i.e.* is bio-based), (2) a plastic material that can be converted to natural substances by microorganisms in the environment (*i.e.* is biodegradable), or (3) a plastic material that features both of the properties (*i.e.* is both bio-based and biodegradable) [17]–[19]. According to the aforementioned definition, bioplastics are classified into three main types as following:

- Type A: both biodegradable and bio-based
- Type B: bio-based but non-biodegradable
- Type C: biodegradable but are produced from fossil fuel resources

This classification is shown on coordinate system in **Figure 2.1**. The horizontal axis shows the biodegradability of the plastic, whereas the vertical axis represents the source of the plastic. Type A, B, and C bioplastics are highlighted in the top right, top left, and bottom right quadrants, respectively. The bottom left quadrant corresponds to the conventional plastics that are derived from fossil fuels and they are neither bio-based nor biodegradable. Type B bioplastics represent the bio-based commodity plastics that are produced from renewable resources but without biodegradability. Most of these plastics such as polyethylene (bio-PE) are made from bioethanol obtained by fermentation of biomass[18]. Due to their non-biodegradability, these plastics can still cause long-term environmental issues and thus cannot be considered as an ideal alternate to the conventional plastics. Type C bioplastics such as polycaprolactone (PCL) are biodegradable but produced from fossil fuels; therefore, they cannot be a sustainable option for replacing the conventional plastics. On the other hand, type A bioplastics such as poly (lactic acid) (PLA) are attractive options to replace conventional plastics due to their renewability and biodegradability.

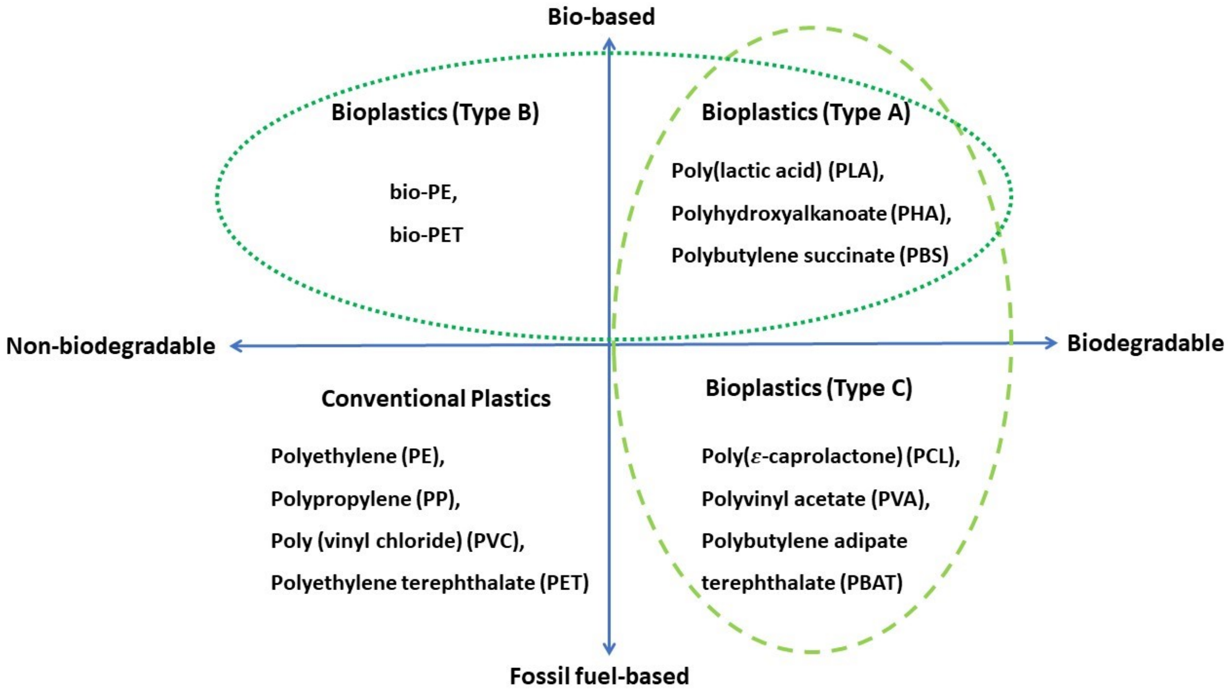

Figure 2.1. Plastics classification in coordinate system proposed in Ref. [17]

2.1.2. Poly (lactic acid) (PLA)

PLA is a linear aliphatic polyester or α-hydroxyalkanoic acid-derived polyester which is made up of lactic acid (2-hydroxy propionic acid) building blocks [19]–[21]. The lactic acid monomer is primarily produced by converting sugar or starch present in renewable resources (e.g. corn, sugarcane, rice, etc.) using bacterial fermentation [9], [20]. Although lactic acid exists in two optically active forms (i.e. D-lactic acid and L-lactic acid), fermentation-derived lactic acid primarily consists of the L form (99.5% of L-isomer) [7], [22]. The polymerization of lactic acid to PLA can be achieved by either direct polycondensation process or ring opening polymerization (ROP) [9], [23]. In the direct condensation process, which is carried out under high vacuum and high temperature, solvents are used to remove the water produced during condensation [6], [9]. This process was first used by Carothers in 1932. The main problem associated with direct polycondensation process is that PLA obtained by this method has a relatively low molecular weight [23]. Alternatively, in the ROP process (shown in **Figure 2.2**), which is a solvent-free method, high-molecular-weight PLA can be obtained by ring opening polymerization of a cyclic dimer of lactic acid (i.e. lactide) [23], [24]. The most common commercial PLA grades include predominantly the L-isomer form, with small content of D-isomer and meso-lactide, made through bulk polymerization using a ROP process [25].

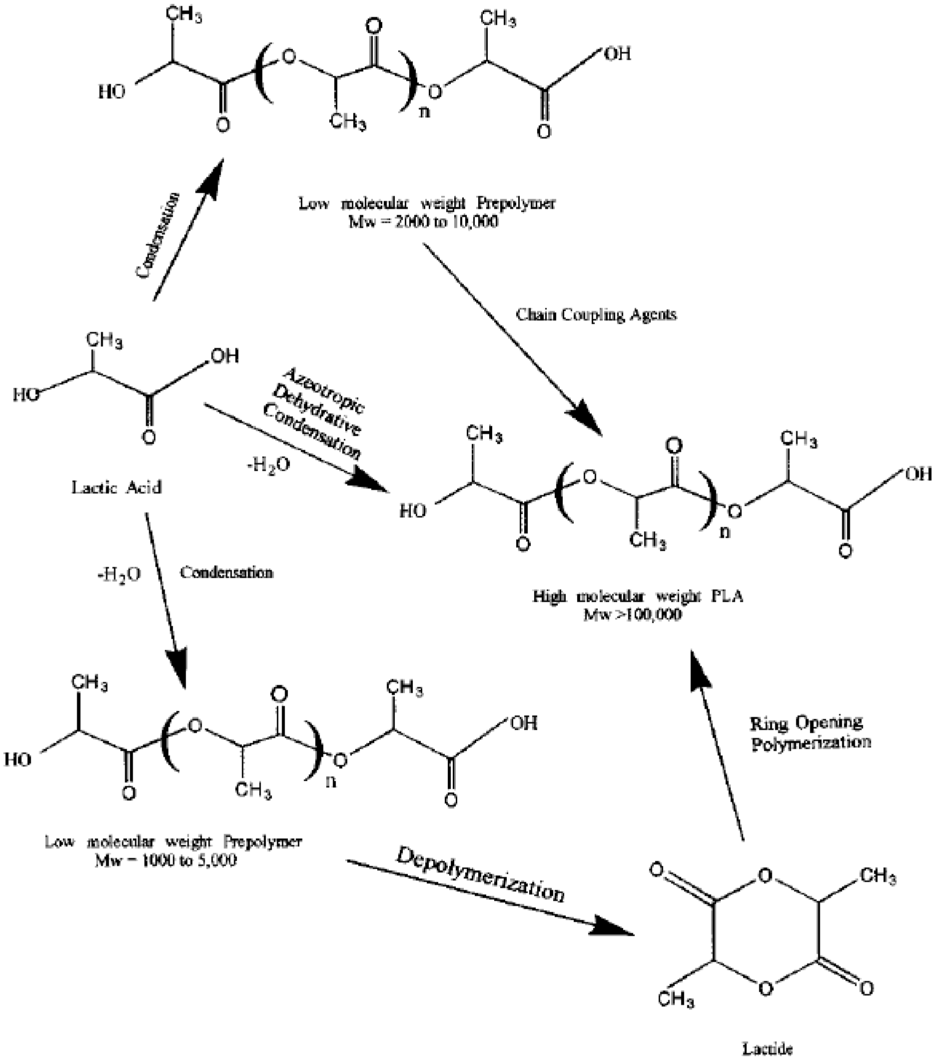

Figure 2.2. Ring opening polymerization (ROP) method for synthesis of high-molecular-weight PLA. Adapted from D. Garlotta [21] by permission of Springer Nature.

2.1.3. General properties of PLA

The properties of a polymer can be categorized into three distinguishable classes: (1) intrinsic properties, which refer to the inherent properties of the polymer itself, further categorized into bulk and molecular properties (e.g. density, glass transition temperatures, crystallinity), (2) processing properties, which determines the behavior of a polymer during forming (e.g. extrusion) and economy of manufacturing of a polymer (e.g. viscosity, melt flow index, melt strength), (3) final product properties, which are determined by the combination of intrinsic and processing properties (e.g. mechanical behavior, heat resistance, water resistance) [26]–[28]. These three classes of properties are interrelated with each other; for instance, an increase in the melting temperature of a polymer (an intrinsic property) is accompanied by an increase in heat resistance (a product property) [29]. Some general properties of a commercial PLA are summarized in **Table 2.1**.

Table 2.1. Characteristics of PLA (grade 4043D) produced by NatureWorks LLC [30]

Characteristics	Amount	Unit
Physical properties:		
Specific gravity	1.24	g/cm^3
Melt flow rate (MFR)	6	g/10 min
Clarity	Transparent	-
Glass transition temperature (T_g)	55-60	°C
Melting temperature (T_m)	145-160	°C
Mechanical properties:		
Tensile strength (σ)	60	MPa
Tensile modulus (E)	3600	MPa
Elongation at break (ε)	6	%

2.2. Applications of PLA

Over the past few years, the interest in utilizing PLA in various fields has grown noticeably due to the modern production techniques that make economical production of PLA viable. The main applications of PLA fall into packaging and medical purposes [31].

2.2.1. Packaging applications

Plastic packaging protects products from moisture, dust, and other adverse external influences while also providing an attractive appearance for the packaged products. Packaging materials can be classified as being intended for either short-term (e.g. food packaging) or long-term use (e.g. electronics and cosmetic containers) [32]. Low water and oxygen permeability, good mechanical properties, and transparency are among the main requirements for a polymer to be used in packaging applications [33]. Currently, most commonly used materials for packaging purposes are poly(ethylene terephthalate) (PET), polyethylene (PE) and polypropylene (PP) due to their low cost, good barrier characteristics and acceptable mechanical properties [32], [33]. The main drawback of these materials is that they are non-degradable and even with current recycling practices, most of the plastic materials used in packaging applications end up as waste after use [33]. Plastic waste can adversely impact the environment if appropriate measures are not considered in their disposal [34]. A reliable, environmentally-friendly disposal process for conventional plastic wastes has not been fully achieved; therefore, the major portion of plastic wastes are simply incinerated or dumped into landfills and oceans [34].

One of the best approaches to reduce both plastic waste and their adverse environmental consequences is to replace the conventional plastics with biodegradable and bio-based biopolymers. PLA is considered to be one of the most promising alternatives to replace conventional plastics, especially in food packaging applications, due to its excellent transparency, renewability, biodegradability, and food safety [23], [32], [35]. In food packaging applications, PLA is an appropriate material for packaging of fresh products whose quality is not susceptible to high oxygen permeability [23]. Recently, PLA containers have been used as “green” packaging for fresh fruit, vegetables, and salads [23]. Furthermore, PLA have been used in other packaging applications such as rigid containers, battery packaging, and bottles [32]. However, the drawbacks associated with PLA, such as poor ductility, high water permeability, and high production cost, have limited its wider use in large-scale commercial applications [32]. Different methods have been proposed to overcome these issues; however, care must be taken to not compromise the biodegradability and biocompatibility of PLA. For instance, numerous studies have reported that incorporation of natural fibers in PLA matrix can improve the mechanical and thermal properties while lowering the cost of the final product due to relatively the lower price of natural fibers compared to majority of biopolymers [36]–[38]. Some other studies suggest that inclusion of plasticizers, particularly the ones that are bio-based and biodegradable, can enhance the flexibility of PLA-based materials without compromising the biodegradability of the final product [13], [14], [39].

2.2.2. Medical applications

In addition to exhibiting biodegradability, biocompatibility, and good processability, PLA is a "bioresorbable polymer" (i.e. a biodegradable polymer that can be degraded under physiological conditions to products which are resorbed within the body [40]), which is a crucial characteristic for many medical applications of polymer materials [23]. Moreover, the ability to tailor PLA's mechanical, chemical, and degradation properties has resulted in a great interest in utilizing PLA in a wide range of medical applications such as stents [41], [42], soft tissue implants [43], spinal cages [44], surgical sutures [45], and drug delivery devices [23]. In the selection of a polymer for medical applications, it is essential to match the mechanical behavior, physical properties, and degradation rate to the requirements of application [40]. For example, in tissue engineering, the scaffolds should have appropriate mechanical properties as well as degradation rate to encourage the regeneration of the tissue [23]. Furthermore, PLA's good biocompatibility and degradation rate makes it an attractive candidate for bone scaffold applications since with the passage of time, PLA gradually disappears from transplantation site, leaving no trace [46].

2.3. Processing of PLA

Proper processing techniques for any polymer need to be used in order to ensure that final product properties of fabricated material match the targeted applications. PLA is a versatile biopolymer which can be processed by both conventional polymer processing technologies (e.g. extrusion, injection molding, blow molding, thermoforming) and advanced processing technologies (e.g. 3D printing, electron beam irradiation) [47]. In some instances, fillers such as natural fibers, plasticizers, and compatibilizers are added to PLA to form blends or composites; processing parameters may need to be adjusted based on the formulation of the material.

2.3.1. Extrusion

Extrusion is the most important continuous melt-processing technique for thermoplastics such as PLA. The extrusion process is usually used as an initial part of the forming machine systems for injection molding, blow molding, and film forming [20]. Inside the extruder is a single-screw or twin-screw which is used for mixing polymers and additives; a typical screw consists of three main sections as shown in **Figure 2.3**: (1) the feed section – which receives the polymer pellets/powder and additives, (2) the transition section – the flight depth gradually decreases in this section in order to improve the polymer-barrel contact, and (3) the meter section – where a constant and shallow flight depth enables accurate metering of the required amount of molten polymer [20]. Both the L/D ratio and the compression ratio are two important screw parameters. The L/D ratio, which is the ratio of flight length of the screw to its outer diameter, controls the residence time and shear of the melt [20]. The compression ratio, which is the ratio of the flight depth in the feed section to the flight depth in the metering section, determines the shear heating provided by the screw [47]. Predominantly, a screw with an L/D ratio of 24 – 30 and compression ratio of 2 – 3 is recommended for PLA processing [20], [48]. For compounding PLA reinforced with fillers, conventional single-screw extruders usually do not provide sufficient dispersion of filler in PLA matrix; therefore, a twin-screw extruder is required to achieve better dispersion of fillers in PLA matrix [20].

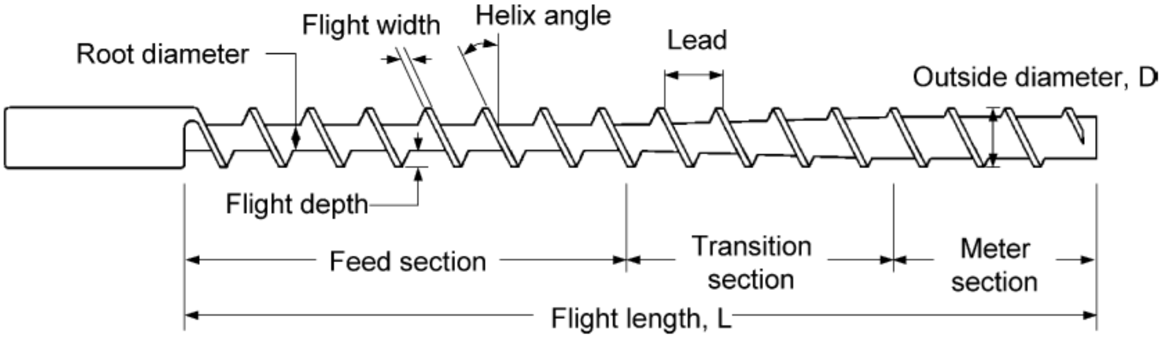

Figure 2.3. Three main sections of a screw for single-screw extruder. Adapted from L.-T. Lim et al. [20] by permission of Elsevier.

2.3.2. Compression molding

Compression molding is a simple composite manufacturing process which is normally used for the fabrication of high-volume composite materials such as automotive components [49]. Generally, there are two types of compression molding processes, i.e. cold compression and hot compression molding. For the purpose of compression molding, composite pellets are usually prepared using an extruder before placing them in the mold cavities. In cold compression molding technique, the curing occurs at room temperature and only pressure is applied to ensure that the material has covered all the cavities, while in hot compression molding, heat is transferred to the composite while applying pressure and the curing process occurs at elevated temperatures [50]. After the curing process, the plastic material is pushed out of the mold.

2.4. Natural fibers and natural fiber-reinforced polymer composites

Natural fibers extracted from plants have attracted a great deal of attention as reinforcing agents in polymer composites over the past decade due to their environmental-friendliness, renewability, and low cost. Natural fibers are generally extracted by a retting (mechanical, dew, and water) process from plant sources [51] and are classified into five basic types: (1) bast fibers (e.g. flax, hemp, jute), (2) leaf fibers (e.g. sisal, abaca), (3) seed fibers (e.g. cotton, coir), (4) fruit fibers (e.g. luffa), (5) grass and reed fibers (e.g. bamboo, wheat, corn) [52]. Natural fibers sourced from plants are primarily composed of cellulose and they all contain hemicellulose, lignin and pectin in their structure [37]. Cellulose is a polysaccharide which normally constitutes major part of natural plant fibers and provides strength and stiffness [53]. Hemicellulose is the second most abundant component of lignocellulosic fibers that is a relatively low-molecular-weight polysaccharide with amorphous structure [54]. Lignin is a complex amorphous polymer that binds the individual fiber cells together [55]. **Table 2.2** shows the comparison of chemical composition of extensively-researched natural fibers. The favorable properties of natural fibers over synthetic fibers such as biodegradability, renewability, excellent mechanical properties, low density, and low toxicity reflect their potential to be utilized in a wide range of applications, especially as bio-based and biodegradable reinforcement in fiber-reinforced polymer composites [52].

Table 2.2. Chemical composition of natural fibers [37], [56], [57]

Fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)
Hemp	70-74	15-20	3.5-5.7	0.8
Sisal	78	10	8	-
Jute	61-72	18-22	12-13	0.2
Ramie	68-76	13-15	0.6-1	1.9-2
Flax	64-72	18-20	2-2.2	1.8-2.3

2.4.1. Hemp

Industrial hemp (*Cannabis sativa*) is an inexpensive annual plant which is cultivated all over the world. In Canada, industrial hemp must contain no more than 0.3% tetrahydrocannabinol (THC) to prevent its use as a narcotic [58]. Hemp fiber is extracted from the bast (i.e. the outer stem tissues) of the hemp plant and is considered as one of the strongest and stiffest natural fibers due to the higher concentration of cellulose in this part of the plant [37]. In addition to the common characteristics of natural fibers, hemp fiber has excellent specific strength and stiffness – comparable to those of glass fibers – and therefore is considered as a favorable reinforcing agent to replace the synthetic fibers in polymer composites [53]. The mechanical and physical properties of hemp fiber are summarized in **Table 2.3**. Additionally, hemp plant contains hurds which comprise the center of the hemp stalk (shown in **Figure 2.4**). Hemp hurds have a lower content of cellulose as compared to hemp fibers; however, they still have the potential to be used as inexpensive reinforcing agents.

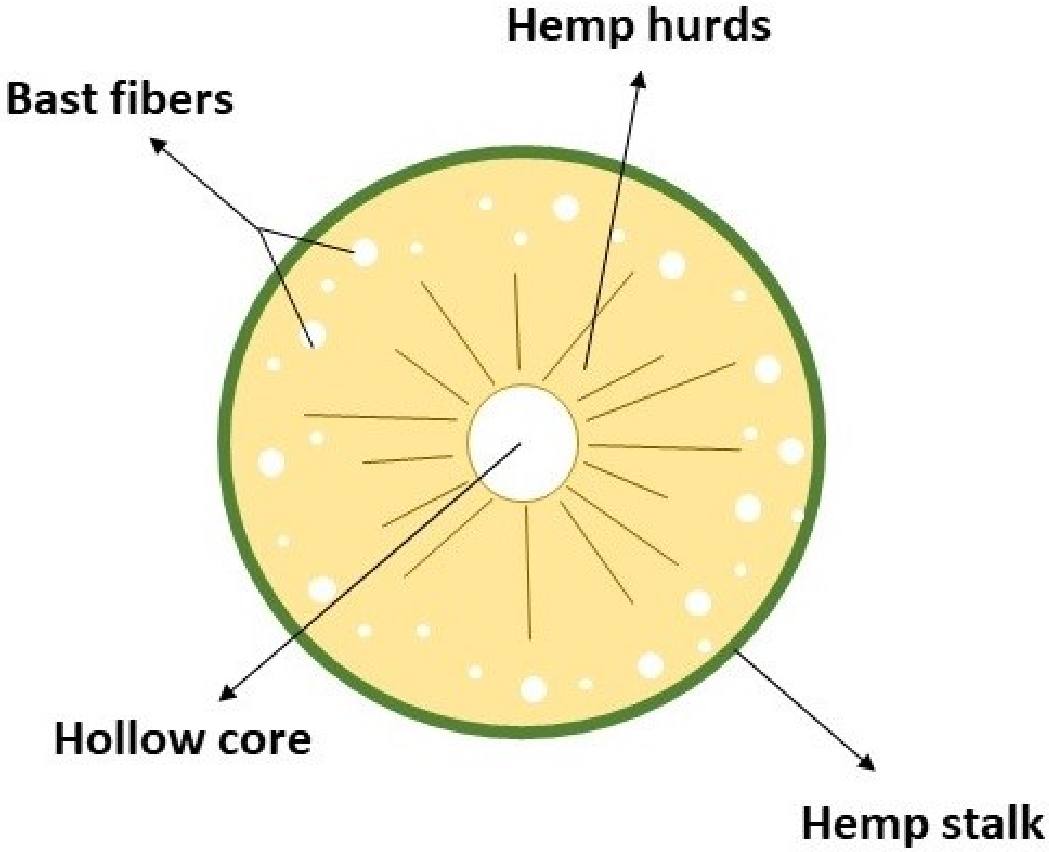

Figure 2.4. Cross-section of hemp stem

Table 2.3. Physical and mechanical properties of hemp fibers [37], [59]

Characteristics	Amount	Unit
Density	1.48	g/cm^3
Moisture content	8	%
Tensile strength	550-900	MPa
Tensile modulus	30-70	GPa
Elongation at break	1.6-4	%

2.4.2. Surface modification of natural fibers

Natural fibers have shown great potential as reinforcing agents in natural fiber-reinforced polymer composites due to their favorable properties. However, natural fibers inherent hydrophilicity which stem from non-cellulosic components (i.e. hemicellulos, pectin, lignin, and wax) compromises the filler-matrix interaction leading to inferior mechanical properties [60]–[62]. To overcome these issues, surface modification of natural fibers using various techniques such as chemical treatments (e.g. alkalization [38], silanization [63]), physical treatments (e.g. plasma [64]), and biological treatments (e.g. enzyme [65]) have been utilized.

Among the aforementioned techniques, chemical treatments of natural fibers is the most commonly explored. In chemical treatments, a chemical reaction occurs between the reactive constituents of natural fibers (e.g. hydroxyl groups) and a chemical reagent which leads to formation of a covalent bond between the two [66]. Alkaline treatments are the most commonly used chemical treatments due to their simplicity and low cost [61], [67]. During an alkaline treatment, hemicellulose, lignin, pectin, and other impurities covering the surface of the natural fibers are partially removed, thereby increasing the surface roughness of the fibers [54]. The increased surface roughness of fibers facilitates the filler-matrix adhesion, which could possibly lead to improved mechanical properties. It has been reported that incorporation of alkaline-treated natural fibers can significantly improve the mechanical and thermal properties of the natural fiber-reinforced polymer composites compared to the sample containing untreated fibers [68]–[70]. For instance, Sawpan et al. investigated the effect of alkaline and silane treatment on the mechanical properties of PLA/hemp fiber composites [61]. They observed that composites containing hemp fibers treated with 5% NaOH solution exhibited higher Young's modulus, tensile strength, and impact strength compared to the composites prepared with either untreated or silane-treated hemp fibers. Sawpan et al. reported that the improvement in mechanical properties of composites comprised of alkaline-treated hemp fibers could be attributed to the removal of hemicellulose and wax from fibers leading to enhanced filler-matrix interaction [61]. However, care must be taken in selecting the alkaline solution concentration as higher concentrations could adversely affect the structure of the natural fibers, and hence the mechanical and thermal properties of the prepared composites. Samaei et al. studied the effect of different NaOH solution concentrations (4, 6, 8, 10 wt %) on the mechanical properties of kenaf fibers [71]. They observed that kenaf fibers treated with 6 wt % NaOH solution showed the highest tensile strength, whereas fibers treated with 10 wt % NaOH solution suffered a substantial decrease in tensile strength compared to untreated fibers. Samaei et al. reported that high concentrations of NaOH solution, such as 10 wt% or higher, may damage the texture of the natural fibers leading to compromised mechanical properties [71].

Hydrogen peroxide (H_2O_2) treatment is an alternative chemical treatment that can be used for surface modification of natural fibers prior to composite fabrication. Hydrogen peroxide is commonly used as bleaching agent for cellulosic materials in industrial applications [72]. It has been reported that bleaching with hydrogen peroxide can effectively remove hemicellulose and lignin from natural fibers leading to improvement in both physical appearance and mechanical properties of fabricated composites [73]. Razak et al. investigated the effect of hydrogen peroxide treatment on the mechanical properties of PLA/kenaf fiber composites. They performed a hydrogen peroxide treatment in an alkaline solution (pH=11) for 60 min at 80 °C. They observed that the mechanical properties – in terms of Young's modulus, tensile strength, and elongation at break – of the composites containing bleached kenaf fibers were significantly improved compared to the composites formed with untreated fibers. Razak et al. reported that the aforementioned improvement can be attributed to the better fiber-matrix interaction caused by removal of hemicellulose and other impurities from surface of the fibers during bleaching [73].

The incorporation of natural fibers in already brittle biopolymer matrices such as PLA could result in further embrittlement of prepared composites. This excessive brittleness limits the wider application of natural fiber-reinforced PLA composites specifically in packaging applications where flexibility of the final product is of great importance. To overcome these challenges, using compatibilizers [74], blending with other ductile polymers [75], and using plasticizers [76] have been proposed. Over the recent years, more interest has been drawn toward using plasticizers that are bio-based, biocompatible, and biodegradable.

2.5. Plasticizers

Plasticizers are low molecular weight substances that are used as additives in polymer industries to improve the flexibility and processibility of polymers [77]. These compounds change the behavior and properties of polymers by reducing polymer-polymer interactions and increasing chain mobility [78]. Usually, the incorporation of a plasticizer to polymer matrix results in a decrease in the glass transition temperature and melting temperature of the formed composite, which provide increased chain mobility and improved processing window, respectively [39], [77].

The use of plasticizer in polymer industries dates back to early 1800s, where camphor and castor oil were used as plasticizing agents for many purposes. Later in the 1900s, phthalic acid esters substituted the other plasticizers and became the most commonly used plasticizers in 21st century [79]. Di(2-ethylhexyl) phthalate (DEHP) has been the most widely used phthalate plasticizer in plastic manufacturing since 1930 due to its desirable properties and low cost [77]. However, in recent years, there have been concerns regarding the health and environmental issues associated with the DEHP. Numerous studies have reported the adverse impacts of DEHP plasticizer on human health associated with the use of this plasticizer in medical or household applications [79]. To overcome the issues related to the phthalate-based plasticizers, more interest has been drawn toward using alternative plasticizers that have lower migration and lower toxicity.

2.5.1 Bio-plasticizers

In addition to the health and environmental issues of phthalate-based plasticizers, newer concerns regarding the effect of plasticizers on the biodegradability and biocompatibility of the biopolymers such as PLA are emerging. Therefore, there is an increasing interest in using bio-plasticizers that are bio-based, biocompatible, and biodegradable. Vegetable oils (VOs) and epoxidized vegetable oils (EVOs) could potentially be used as alternatives in the polymer industry.

Vegetable oils (VOs) are derived from plants and consist of different triacylglycerols (triglycerides) [80]. Triacylglycerol is an ester composed of a glycerol molecule and three fatty acids, as shown in **Figure 2.5**. VOs are considered a feasible alternative to petroleum based plasticizers due to their biodegradability, renewability, low toxicity, and low cost [81]. Most of the VOs have high content of unsaturated fatty acids which limits their reactivity and hence miscibility in polymer matrices [82]. To overcome this drawback, carbon double bonds of unsaturated fatty acids in the VOs can be transformed into epoxy fatty acids using different epoxidation methods.

The epoxide groups (also known as oxirane groups) present in the epoxidized vegetable oils (EVOs), enhance the reactivity of EVOs with carbonyl and hydroxyl groups of polymer matrices such as PLA [83]. Numerous studies have reported the effect of epoxidation of vegetable oils on properties of plasticized polymers. In these materials, the incorporation of epoxide groups leads to reduced migration of the plasticizer (compared with non-epoxidized oils). For instance, Orue et al. studied the effect of epoxidation of linseed and soybean oils on mechanical and thermal properties of PLA [84]. They observed that samples containing epoxidized oils showed higher tensile strength and elongation at break as compared to the samples plasticized with non-epoxidized oils. They also reported that samples with non-epoxidized oils showed similar thermal stability as neat PLA, while using epoxidized oils led to slight reduction in thermal stability of the samples.

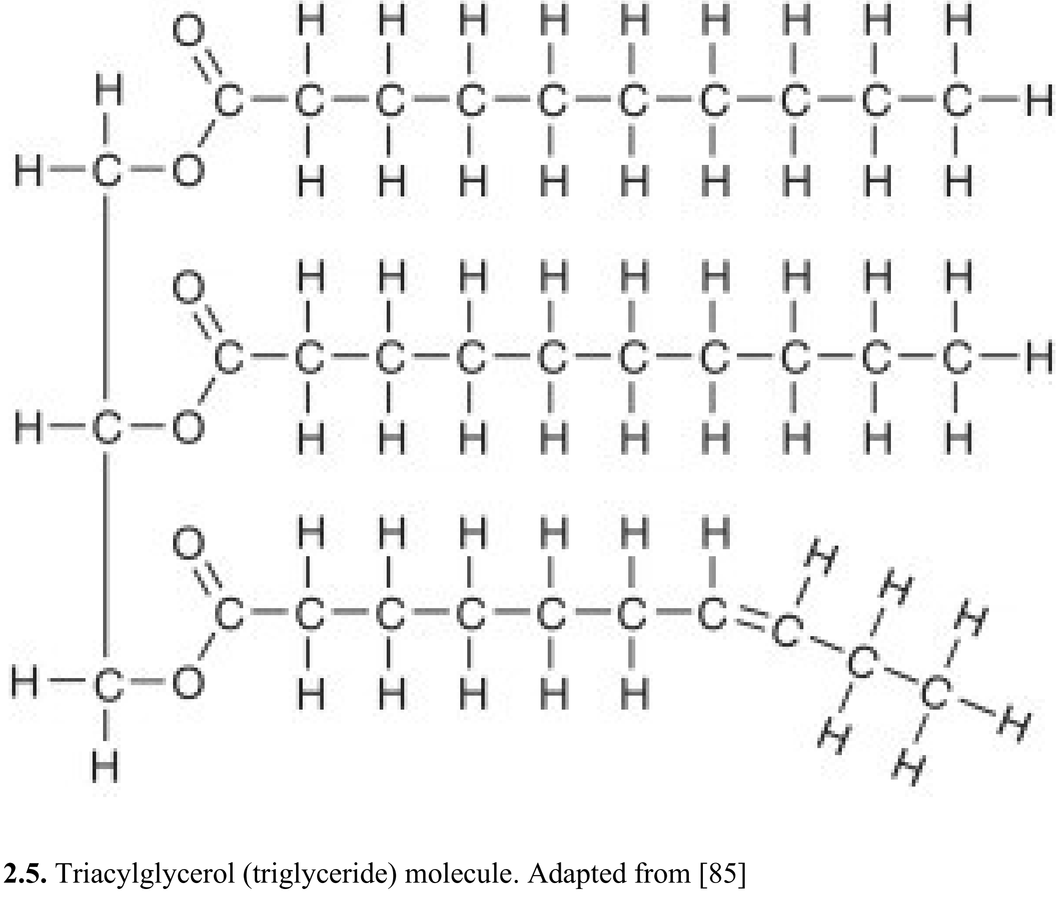

Figure 2.5. Triacylglycerol (triglyceride) molecule. Adapted from [85]

It has been reported that EVOs can enhance the compatibility of lignocellulosic fibers with PLA matrix by reacting with the hydroxyl groups present in both PLA and natural fibers [86], [87]. Balart et al. investigated the effect of epoxidized linseed oil (ELO) on the mechanical and thermal properties of hazelnut shell flour (HSF) reinforced PLA composites [86]. Their SEM results showed a remarkable improvement in the interfacial adhesion between HSF and PLA matrix for the samples containing more than 7.5 wt % ELO. They inferred that these interactions contributed to lowering the fragility of the samples by increasing the elongation at break. They reported that the highest elongation at break value (17.1%) was observed for the sample containing 22.5 wt % ELO, while the PLA/HSF composites without ELO had an elongation at break value of 3.1%. Their thermogravimetric analysis indicated that increasing ELO content in the PLA/HSF/ELO ternary system contributed to improving the thermal stability of the samples.

Similarly, epoxidized canola oil (ECO) is a vegetable-based oil that is sourced from canola plant, which is widely grown in Alberta, Canada. ECO is a bio-based, biodegradable, and non-toxic material that has the potential to be used as a bio-plasticizer in polymer materials, especially in biopolymers such as PLA. ECO can be obtained from low-value canola oil, which makes it an attractive alternative to relatively expensive petroleum-based plasticizers.

3. The effects of alkaline and alkaline/peroxide treatments on the mechanical and thermal properties of PLA/hemp hurd powder biocomposites[1]

Abstract

Sourced from agricultural waste, hemp hurds are renewable materials with high strength that pose huge potential in natural fiber reinforced polymer biocomposites. However, as for many plant fibers, the inherent hydrophilicity of hemp hurds leads to inferior filler-matrix interfacial interactions, compromising the mechanical properties of the resulting biocomposites. In this study, two chemical treatments, alkaline (NaOH) and alkaline/peroxide ($NaOH/H_2O_2$) were employed to treat hemp hurds to improve their miscibility with poly(lactic acid) (PLA) for the formation of biocomposites. The effects of reinforcement content (5, 10, and 15 wt %), chemical treatments (purely alkaline vs. alkaline/peroxide) and treatment cycles (1 and 3 cycles) on the mechanical and thermal properties of the biocomposites were investigated. The biocomposites of treated hemp hurd powder exhibited enhanced thermal stability in the temperature range commonly used to process PLA (130-180 °C). The biocomposites containing 15 wt % hemp hurd powder prepared using a single-cycle alkaline/peroxide treatment (PLA/15APHH1) exhibited a Young's modulus of 2674 MPa, which is 70% higher than that of neat PLA and 9.3% higher than that of biocomposites comprised of PLA containing the same wt % of untreated hemp hurd powder (PLA/15UHH). Furthermore, the tensile strength of the PLA/15APHH1 biocomposite was found to be 62.6 MPa, which was 6.5% lower than neat PLA and 23% higher than the PLA/15UHH sample. The results suggest that the fabricated PLA/hemp hurd powder biocomposites have great potential to be utilized in green and sustainable packaging applications.

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[1] A version of this chapter has been submitted for publication.

3.1. Introduction

Environmental issues associated with both plastic waste and depletion of petroleum resources have been a major driving force for the production and utilization of biodegradable biopolymers. Among biodegradable biopolymers, poly(lactic acid) (PLA) is attractive for a variety of applications owing to its biocompatibility [88], renewability [23], and promising mechanical properties [89], [90]. Despite these key advantages, PLA has had only limited adoption in fields such as packaging, automotive industry, and construction, mainly because of some crucial drawbacks including brittleness, low thermal stability, and relatively high production cost. Incorporation of reinforcing agents, plasticizers, and compatibilizers are among the proposed strategies to tailor or enhance the properties of PLA [76], [91]–[94].

In recent years, natural fiber-reinforced biopolymers have received extensive interest due to the "green" nature of these biocomposites. Moreover, natural fibers have positive characteristics including desirable mechanical properties, low density, and low cost, which make them a promising candidate as reinforcing fillers [37], [95]. Among reinforcing agents, hemp fiber accounts for one of the most extensively studied natural fibers in the literature. Derived from the hemp plant, hemp fiber (also called bast fiber) is rich in cellulose (70-74%) and is known as one of the stiffest and strongest natural fibers available for industrial use, and thus is considered as a desirable reinforcing material [37]. Bast fibers, which grow on the outer core of the hemp stalk, can be meters in length, and are one of the most highly valued parts of the plant. The hemp plant additionally includes hurds, the lightweight soft woody core of the hemp plant, which are often considered to be waste, and are therefore lower in cost than bast fibers. Hemp hurds also have a high cellulose content (40-48%), and therefore cellulose extracted from hurd is still a good candidate for use as a reinforcing agent in polymers [96], [97]. However, like other natural fibers, hemp hurds also contain non-cellulosic components such as hemicellulose, lignin, pectin, and wax; these components tend to have low thermal stability and high hydrophilicity, which may result in poor filler-matrix interfacial interaction as well as inferior processibility during the formation of biocomposites [11], [67], [98]. To overcome these challenges, surface modification of natural fibers through chemical treatments (e.g. alkalization [99], silanization [63], acetylation [100]), physical treatments (e.g. plasma [64], [101] and thermal steam explosion [102]), and biological treatments (e.g. enzyme [65]) are typically performed before biocomposite processing.

Among surface modification techniques, chemical treatments of natural fibers have been studied extensively in the last few years. Alkaline treatment is a common chemical treatment to remove non-cellulosic constituents from natural fibers due to its simplicity and low-cost [67], [103]. Numerous studies have reported superior mechanical and thermal properties of composites containing fibers pretreated with alkaline solutions as compared with composites containing untreated fibers [36], [38], [70]. For instance, Sawpan et al. observed that the incorporation of hemp fibers treated with 5 wt % NaOH solution in a PLA matrix increased the Young's modulus, tensile strength, and impact strength of biocomposites as compared with composites containing either untreated or silane-treated fibers [61]. Sawpan et al. inferred that the aforementioned improvements could be attributed to a strong fiber-matrix interfacial interaction caused by the removal of hemicellulose and impurities from fiber surface after alkaline treatment. However, it should be noted that higher concentrations of NaOH might result in the degradation of fibers which can adversely affect the mechanical and thermal properties of the reinforced composites. Pickering et al. evaluated the impact of alkaline treatment on the mechanical properties of hemp fibers [104]. Their results indicated that using 15 wt % NaOH solution for treatment purposes adversely affected the strength of fibers as a consequence of excessive delignification and degradation of cellulose.

Bleaching with hydrogen peroxide (H_2O_2) is an alternative chemical treatment that is extensively used in the textile industry [105]. It has been reported that hydrogen peroxide treatment can improve both the physical appearance and mechanical properties of fibers due to the partial removal of lignin [73]. To increase the efficiency of bleaching, it is crucial to perform the hydrogen peroxide treatment in an alkaline medium [106]. Zhang et al. evaluated the effect of alkaline/peroxide treatment on the properties of citrus dietary fibers by dispersing the fibers in 1% hydrogen peroxide solution with 0.5 M NaOH solution. They observed that after alkaline/peroxide treatment, lignin and pectin contents were reduced and the treated fibers were found to be richer in cellulose [107]. In another study, Razak et al. investigated the impact of alkaline/peroxide treatment (5% v/v) on the mechanical properties of PLA/kenaf biocomposites. They reported that the biocomposites formed with the bleached fibers showed higher tensile strength, Young's modulus, and elongation at break compared to biocomposites containing unbleached fibers [73]. However, the effect of multiple cycles of treatment was not investigated by any of these studies.

One obstacle to the wide-spread use of PLA in packaging and other single-use applications is cost; if the cost of this polymer can be reduced through the incorporation of an inexpensive, biodegradable filler without compromising the properties of the material overall, PLA may find more widespread applications. Most of the studies in the literature used bast fibers (valuable and relatively expensive part of plants) as reinforcing agents for PLA-based biocomposites, while very few studies have reported the use of hemp hurds.

In this work, we prepare PLA/hemp hurd powder biocomposites, and characterize their thermal and mechanical properties as a function of hemp hurd powder treatment and concentration. Hemp hurd powder is prepared by grinding hemp hurds to obtain a powder with a size of less than 500 microns. The hemp hurd powder is subjected to two different types of chemical treatments (alkaline and alkaline/peroxide), which were selected to achieve good interactions between the inherently hydrophilic hemp hurds [53] and the hydrophobic PLA [23] matrix. These treatments are expected to remove the undesirable components (i.e. hemicellulose, lignin, pectin, and wax) of the hemp hurds, thereby increasing the cellulose fraction of the material. While increasing the number of treatment cycles may reduce the fraction of undesirable components and enhance the fraction of cellulose in the resulting material, too many cycles may actually damage the hemp hurds. We therefore examine how the properties of both hemp hurds and of PLA/hemp hurd powder biocomposites are impacted by repeating multiple cycles of these treatment processes. Overall, the effects of the type of chemical treatment, number of treatment cycles, and hemp hurd powder content on the mechanical and thermal properties of the fabricated PLA/hemp hurd powder biocomposites are investigated, toward developing a material that can be used in packaging industry, especially in applications which require relatively stiff materials.

3.2. Materials and Methods

3.2.1. Materials

Poly(lactic acid) (PLA, nominal Mw: 390 kDa, grade 4043D pellets) was purchased from NatureWorks LLC, Minnetonka, MN, USA. Hemp hurds were provided by the Vegreville Decortication Facility, Vegreville, AB, Canada. Required chemicals such as sodium hydroxide (NaOH) pellets (relative density: 2.13 g/cm^3 at 20 °C, purity: ≥98%) and hydrogen peroxide (H_2O_2) solution (30 wt %, relative density: 1.11 g/cm^3) were purchased from Sigma Aldrich®, Oakville, ON, Canada, and used as received without any processing.

3.2.2. Preparation of hemp hurd powders

The visible dirt of the received hemp hurds was removed by vigorous washing with 60 °C water for 2 h. After drying at 90 °C for 24 h, washed hemp hurds were ground using a blade coffee grinder for 3 min; the resulting powder was sieved using a 500 µm size screen. This material was denoted as untreated hemp hurd powder (UHH). Once prepared, the ground hurds are stored in sealed Ziploc at room temperature until their use.

3.2.2.1. Alkaline treatment

The alkaline treatment starts with sonicating 5 g of ground hemp hurds in 300 ml of distilled water for 30 min to dissolve water-soluble hemicellulose. Afterward, the mixture was vacuum filtered using a 20 µm size screen. The filtered wet powder was then put in 100 ml of 8 wt % NaOH solution and sonicated at room temperature for 1 h. The solution was then kept at room temperature (without sonication) for 47 h. Then, the sample was vacuum filtered using a 20 µm size screen and washed with distilled water containing 1% acetic acid to neutralize the remaining caustic soda, and then thoroughly washed with distilled water until the pH of ~7 was reached. Finally, the hurd powder was dried at 90 °C for 24 h. The resulting powder was denoted as single-cycle alkaline-treated hemp hurd powder (AHH1). The same treatment procedure was repeated twice more to obtain three-cycle alkaline-treated hemp hurd powder (AHH3).

3.2.2.2. Alkaline/peroxide treatment

After washing and vacuum-filtering of 5 g of hemp hurd powder using the procedure explained in the alkaline treatment section (2.2.1), the wet powder was added to 100 ml of 8 wt % NaOH solution and sonicated at room temperature for 10 min. Then, 100 mL of 11% v/v hydrogen peroxide solution was added in the mixture, which was vigorously stirred for 90 min at room temperature. This treatment process was inspired by Zhang et al., where they observed that performing alkaline hydrogen peroxide treatment improved the properties of citrus dietary fiber [107]. The sample was then filtered and washed with distilled water until a pH of ~7 was reached. Finally, the powder was dried at 90 °C for 24 h. The complete cycle includes both alkaline and hydrogen peroxide treatments, and the obtained powder is referred to as single-cycle alkaline/peroxide-treated hemp hurd powder (APHH1). In some cases, the same, two-part treatment procedure was repeated twice more to prepare three-cycle alkaline/peroxide-treated hemp hurd powder (APHH3). The images corresponding to untreated and treated hemp hurd powders are shown in Appendix A, **Figure S1**.

3.2.3. Biocomposite fabrication

Before biocomposite fabrication, hemp hurd powder and PLA were dried at 70 °C in an oven overnight to minimize the moisture content. The compounding was carried out in a co-rotating twin-screw extruder (HAAKE™ Minilab II micro compounder, Thermo Fisher Scientific, Waltham, MA, USA) at 160 °C with a rotor speed of 75 rpm. All batches were cycled through the extruder channel for 3 min (the residence time) to ensure proper melt-mixing and then extruded through a rectangular nozzle. The extruded filaments were cooled to room temperature and then pelletized manually using scissors. The resulting pellets were rectangular in shape, typically 2 – 3 mm in length, 2 mm in width, and 0.5 – 1 mm in thickness. As per the ASTM D638-14 test [108], standard Type I test specimens were prepared using a hot-pressing machine (Model 4386, Carver Inc., Wabash, IN, USA) and a rectangular steel mold 2 mm thick with dimensions of 70 mm × 80 mm. Samples were maintained under 2 MPa pressure at 180 °C for 5 min (these parameters were selected to minimize the number of bubbles that formed in the samples). Once cooled down to room temperature, dumbbell-shaped specimens were removed out of the mold and stored in a sealed bag before tensile testing. The schematic of the dumbbell-shaped specimen is shown in Appendix A, **Figure S2**.

Throughout this work, each biocomposite is referred to in the format of "PLA/filler type", where the number before the filler type refers to hemp hurd powder content; for instance, PLA/15APHH3 denotes PLA/hemp hurd powder biocomposites containing 15 wt % of three-cycle alkaline/peroxide-treated hemp hurd powder. The designated names for hemp hurd powders and prepared biocomposites are summarized in **Table 3.1**.

Table 3.1. Designated names for hemp hurd powders and prepared biocomposites

Biocomposites	Filler loading (wt %)	Filler type	Type of treatment	Number of cycles of treatment
PLA/5UHH	5	UHH	Untreated	-
PLA/5AHH1	5	AHH1	Alkaline	1
PLA/5AHH3	5	AHH3	Alkaline	3
PLA/5APHH1	5	APHH1	Alkaline/peroxide	1
PLA/5APHH3	5	APHH3	Alkaline/peroxide	3
PLA/10UHH	10	UHH	Untreated	-
PLA/10AHH1	10	AHH1	Alkaline	1
PLA/10AHH3	10	AHH3	Alkaline	3
PLA/10APHH1	10	APHH1	Alkaline/peroxide	1
PLA/10APHH3	10	APHH3	Alkaline/peroxide	3
PLA/15UHH	15	UHH	Untreated	-
PLA/15AHH1	15	AHH1	Alkaline	1
PLA/15AHH3	15	AHH3	Alkaline	3

PLA/15APHH1	15	APHH1	Alkaline/peroxide	1
PLA/15APHH3	15	APHH3	Alkaline/peroxide	3

3.2.4. Characterization

3.2.4.1. Fourier transform infrared spectroscopy (FT-IR)

The chemical analysis of untreated and treated hemp hurd powders was performed using an FTIR spectrometer (MB3000, ABB Inc., Zurich, Switzerland) equipped with ATR (attenuated total reflectance) to determine the interfacial bonds. Each spectrum was obtained in the spectral range of 4000 cm^{-1} to 400 cm^{-1} with a scanning resolution of 4 cm^{-1}. A total number of 120 scans were taken for each sample and averaged.

3.2.4.2 Scanning electron microscopy (SEM)

The morphological analysis of untreated and treated hemp hurd powders was carried out using SEM analysis (Model ZEISS EVO MA 10, Jena, Germany). Samples were placed on the aluminum holders with double-sided conductive tape. Prior to carrying out SEM characterization, a Denton sputter unit was used to coat the samples with a thin layer of gold.

3.2.4.3. X-ray diffraction (XRD) analysis

The X-ray powder diffraction analysis of untreated and treated hemp hurd powders was performed using an X-ray diffractometer (Bruker XRD D8 Discover, Billerica, MA, USA). The diffracted intensity was recorded at a scanning rate of 0.5°/min between 5° and 40° diffraction angle at 40 kV and 30 mA using locked couple mode. The crystallinity index (I_C) was calculated using the Segal method [109], where I_{002} is the peak intensity of diffraction at 2θ angle close to 22.5° and I_{am} is the peak intensity of the amorphous phase of hemp hurd powder at 2θ angle close to 18.7°. The Segal method is a simple method that provides a good estimation of the crystallinity index of powder samples, and is expressed in the form of equation (1):

$$I_C\ (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

3.2.4.4 Thermo-gravimetric analysis (TGA)

The thermal stability of the hemp hurd powders and biocomposites was investigated using TGA (TGA/DSC Model 1, Mettler Toledo, Columbus, OH, USA) equipped with an ultra-micro balance cell and differential thermal analysis (DTA) sensors. Around 10 mg sample was placed in an alumina crucible and heated from 25 °C to 799 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with a flow rate of 20 mL/min.

3.2.4.5. Differential scanning calorimetry (DSC)

Thermal analysis and crystallization behavior of PLA and the biocomposites were investigated by use of a differential scanning calorimeter (DSC Model 1, Mettler Toledo, Columbus, OH, USA). Samples with a mass of approximately 5 mg were placed in sealed aluminum crucibles and then heated from -20 °C to 200 °C at a heating rate of 5 °C/min. Following the first heating scan, samples were held at 200 °C for 5 min and then cooled down to -20 °C at a cooling rate of 5 °C/min. Finally, samples were heated again to 200 °C at a heating rate of 5 °C/min to obtain the second heating cycle behavior. The degree of crystallinity (X_c) of PLA and its biocomposites were calculated using the equation (2):

$$X_c\ (\%) = \frac{\Delta H_m}{w \times \Delta H_m^0} \times 100 \quad (2)$$

Where w is the weight fraction of PLA in the biocomposites, ΔH_m corresponds to the melting enthalpy of biocomposite, and ΔH_m^0 refers to melting enthalpy of pure crystalline PLA (96 J/g) [76].

3.2.5. Mechanical testing of biocomposites

Tensile properties of PLA and the biocomposites were evaluated according to ASTM D638, using a universal testing machine Instron 5943 (Instron, Norwood, MA, USA) equipped with a 1 kN load cell at a crosshead speed of 5 mm/min. A thin layer of rubber was placed in between the grip area and clamps to prevent slipping during the experiment. Clamps were carefully tightened by hand to avoid over-clamping of the sample. At least 5 samples were measured for each composite type and the average value is reported. The total length, gauge length, width, and thickness of the dumbbell-shaped specimens were 75 mm, 25 mm, 4 mm, and 2 mm, respectively. Fabricated dumbbell-shaped specimens after tensile testing are shown in Appendix A, **Figure S3**.

3.3. Results and discussion

3.3.1. FTIR analysis

FTIR spectra of untreated, alkaline, and alkaline/peroxide treated hemp hurd powders are shown in **Figure 3.1**. The characteristic peaks are located at the following wavenumbers: 3335 cm^{-1} (OH stretching in cellulose, hemicellulose) [11], 1734 cm^{-1} (C=O stretching of acetyl groups in hemicellulose) [98], 1239 cm^{-1} (C-O stretching of acetyl groups in lignin) [110], 1158 cm^{-1} (asymmetrical C-O-C stretching in cellulose, hemicellulose) [111], 1055 cm^{-1} (C-OH vibration in cellulose) [112], 896 cm^{-1} (symmetrical β-glycoside bonds ring-stretching in cellulose) [111]. It can be inferred from **Figure 3.1** that the chemical composition of the hemp hurd powder changed after alkaline and alkaline/peroxide treatment since the peaks present in untreated hemp hurd powder (UHH) at 1734 cm^{-1} and 1239 cm^{-1} – corresponding to hemicellulose and lignin, respectively – were thoroughly reduced in the spectra of treated hemp hurd powders, indicating the removal of hemicellulose and lignin. Similar FTIR results have already been reported in other studies. For instance, Oza et al. and Sgriccia et al. studied the impact of alkaline and silane treatment on the properties of hemp fibers [67], [113]. Each of the studies reported similar changes in the peaks located at 1750 – 1730 cm^{-1} and 1250 cm^{-1}, indicating the removal of hemicellulose and lignin after chemical treatments.

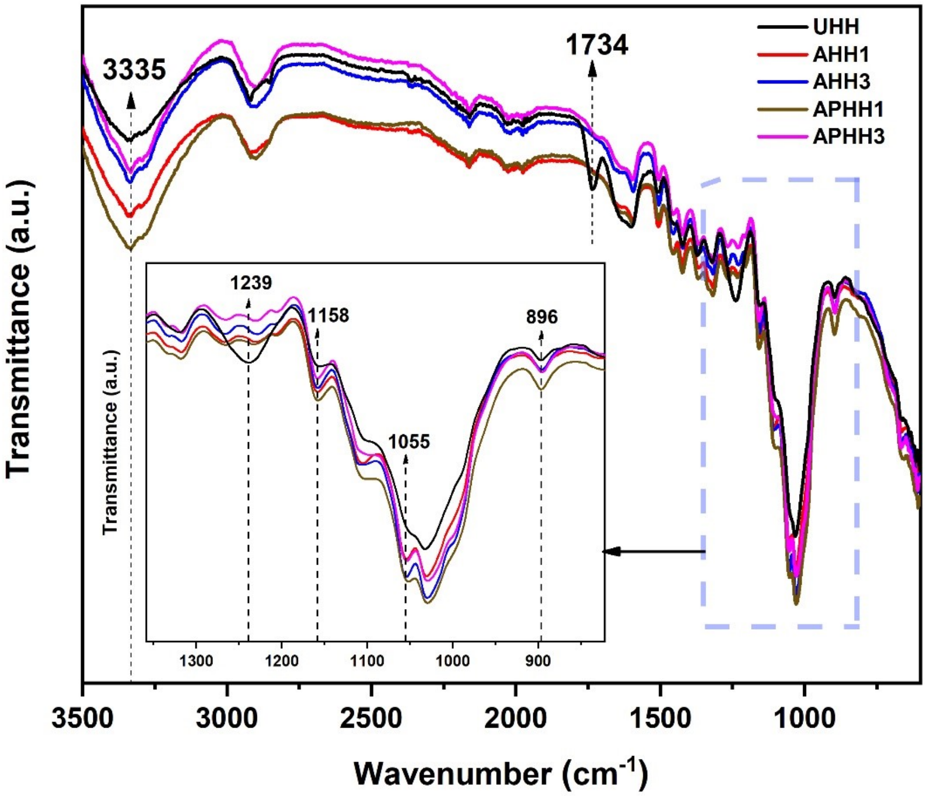

Figure 3.1. FTIR spectra of untreated and treated hemp hurd powders

3.3.2. SEM analysis

The effect of alkaline and alkaline/peroxide treatments on the morphology of the hemp hurd powder can be seen by comparing the SEM images of untreated and treated hemp hurd powders shown in **Figure 3.2**. The impurities covering the surface of untreated hemp hurd powder (**Figure 3.2** (a)) including wax, hemicellulose, and lignin, account for the smooth surface. For hemp hurd powder samples exposed to chemical treatment, a rougher surface texture is visible, which can be attributed to the fibrillation during treatment process. Interestingly, the degree of surface roughness of the hemp hurd powder increases when performing multiple treatment cycles. For instance, **Figure 3.2** (b) and (d) shows the mild surface roughness of hemp hurd powder after only one cycle of treatment. In contrast, **Figure 3.2** (c) and (e) shows higher surface roughness of hemp hurd powder resulting from three-cycle alkaline and alkaline/peroxide treatments, respectively. The increasing roughness visible with increasing number of treatment cycles suggests that either (1) the hemicellulose and lignin are being removed more completely by multiple cycles, or (2) that the cellulose itself may be damaged by increasing number of treatments. The complete removal of lignin or damage to the cellulose fibers could result in etched surfaces, which may compromise the mechanical properties of biocomposites formed with three-cycle treated hemp hurd powders(as will be discussed later in the chapter).

The results of the alkaline treatment (which uses an 8 wt % NaOH solution) are in agreement with the literature. Kathirselvam et al. treated raw cellulose fibers with 2 wt %, 5 wt %, and 8 wt % of NaOH solution for 60 min at room temperature [114]. They observed that while a mild concentration (2 wt %) of alkaline solution did not noticeably alter the surface of the fibers, fibers treated with 5 wt % and 8 wt % had rougher surface attributable to the complete removal of wax and impurities.

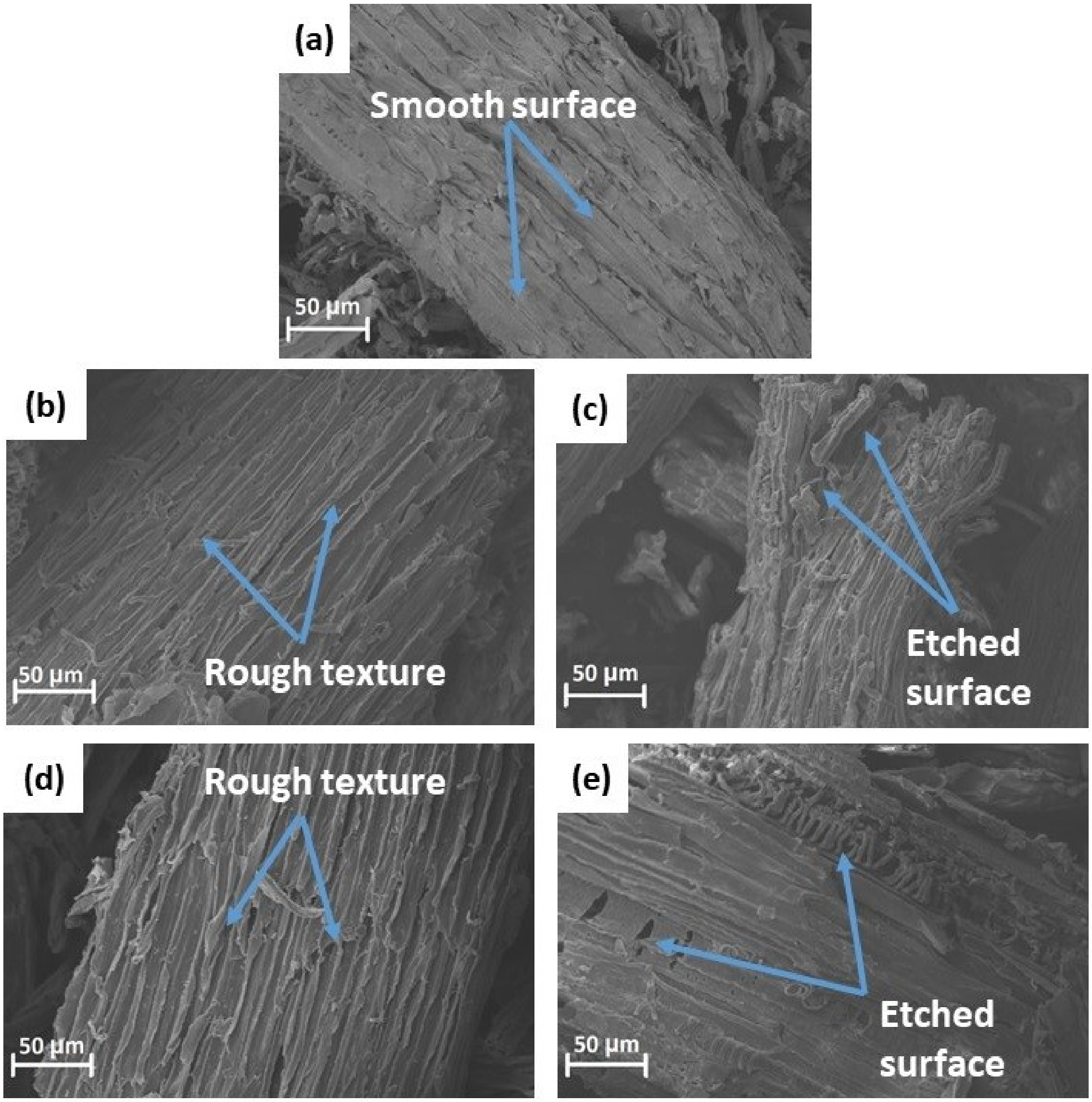

Figure 3.2. SEM micrographs of untreated hemp hurds (a), treated hemp hurds exposed to one and three cycles of alkaline treatment (b and c, respectively), and hemp hurds exposed to one and three cycles of alkaline/peroxide treatment (d and e, respectively).

3.3.3. XRD

The XRD patterns of untreated, alkaline, and alkaline/peroxide treated hemp hurd powders are presented in **Figure 3.3**. The characteristic peak of crystalline cellulose is located at $2\theta = 22.5°$; this peak is largest in magnitude for hemp hurd powder treated with three cycles, indicating that these samples have a high fraction of cellulose with respect to other components. On the other hand, for untreated hemp hurd powder, this peak is smaller in magnitude and shifted to a slightly lower angle, indicating that these samples have a lower overall fraction of cellulose. For hemp hurd powder which has undergone a single-cycle treatment, this peak exhibits an intermediate height and angle, indicating that these samples have an intermediate fraction of cellulose.

In terms of the type of treatment, hemp hurd powder treated with alkaline/peroxide solution exhibited peaks with larger magnitude at $2\theta = 22.5°$ compared to the alkaline-treated hemp hurd powder, indicating that the combined treatment is more effective at removing non-cellulosic components. For all samples, other noticeable peaks are observed at 2θ angles around 14.8°, 16.2°, and 34.5° corresponding to the crystallographic planes $(1\ \bar{1}\ 0)$, $(1\ 1\ 0)$, and $(0\ 0\ 4)$, respectively [98], [115]. The crystallinity index of each type of hemp hurd powder was calculated using the Segal method, and the results are summarized in **Table 3.2**. The results revealed that the crystallinity index of hemp hurd powder increased after performing alkaline and alkaline/peroxide treatments, where increasing the number of treatments resulted in a higher crystallinity index for each type of treatments. Moreover, hemp hurd powder which was treated using three cycles of alkaline/peroxide treatment (APHH3) exhibited the highest crystallinity index ($I_C = 53.28\%$), corresponding to an approximately two-fold increase in crystallinity with respect to untreated hemp hurd powder (UHH). The increased crystallinity index of treated hemp hurd powders can be attributed to the removal of amorphous content of hemp hurd powder including hemicellulose, lignin, and pectin during treatments which facilitated the rearrangement of cellulose chains [116]. Similar results regarding the crystallinity index of single-cycle alkaline-treated natural fibers have already been reported in other studies [11], [110], [117]. For instance, Vijay et al. observed a similar trend in crystallinity index of alkaline-treated fibers owing to the removal of amorphous constituents, resulting in relaxation of cellulose chains [110].

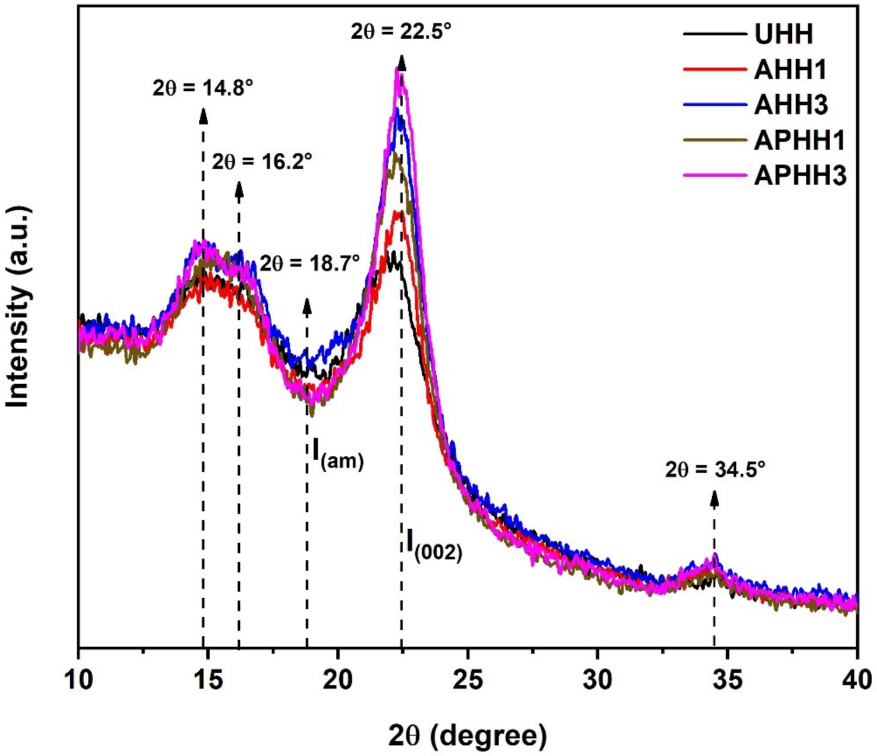

Figure 3.3. XRD patterns of untreated and treated hemp hurd powders

Table 3.2. The crystallinity index of untreated and treated hemp hurd powders

Sample	UHH	AHH1	AHH3	APHH1	APHH3
Crystallinity index (%)	27.1	40.2	42.6	39.7	53.3

3.3.4. Thermal stability of hemp hurd powders

TGA results of alkaline and alkaline/peroxide treated hemp hurd powders are shown in **Figure 3.4** (a) and (b), respectively. T_{10}, corresponding to the temperature at which 10% weight loss has occurred, and T_{50}, the temperature at which 50% weight loss has occurred, were used as the reference parameters to evaluate the thermal stability of the hemp hurd powders. Extracted T_{10} and T_{50} values of untreated and treated hemp hurd powders are summarized in **Table 3.3**. It can be inferred from **Table 3.3** that both T_{10} and T_{50} values increased for treated hemp hurd powders, indicating that the thermal stability of the treated hemp hurd powders increased in comparison to the untreated hemp hurd powder. This might be due to the removal of thermally unstable contents of hemp hurd powder such as hemicellulose, pectin, and wax during the treatments [98], [110], [118]. Moreover, in both of the treatments, an increase in the number of treatments further increased the T_{10} values of the hemp hurd powders, indicating continued removal of hemicellulose and pectin during the successive treatments.

The derivative of thermogravimetric (DTG) thermograms of alkaline and alkaline/peroxide treated hemp hurd powders are presented in **Figure 3.4** (c) and (d), respectively. For all samples, the first decomposition peak was detected between ambient temperature and 115 °C, which is associated with the removal of water content from hemp hurd powder [11]. This peak was observed for all of the hemp hurd powders, however, untreated hemp hurd powder (UHH) experienced a higher mass loss in this range than treated hemp hurd powders, revealing the fact that more water was absorbed by UHH due to their higher hydrophilicity. For UHH, a second decomposition peak was observed at 280 °C, which could be linked to the degradation of hemicellulose and partly lignin, which is in accordance with the results reported by Kabir et al. [119]. This peak was not observed for treated hemp hurd powders, reflecting that the hemicellulose was effectively removed during alkaline and alkaline/peroxide treatments. The main decomposition peak of both untreated and treated hemp hurd powders occurred in the range from 320 °C – 400 °C, which accounts for the decomposition of cellulose content in the hemp hurds. Maximum mass loss of UHH was observed at 356 °C, while this peak shifted to 374 °C and 369 °C for AHH3 and APHH3 samples, respectively. This observation indicates that the components with lower thermal stability were removed during three cycles of each treatment type.

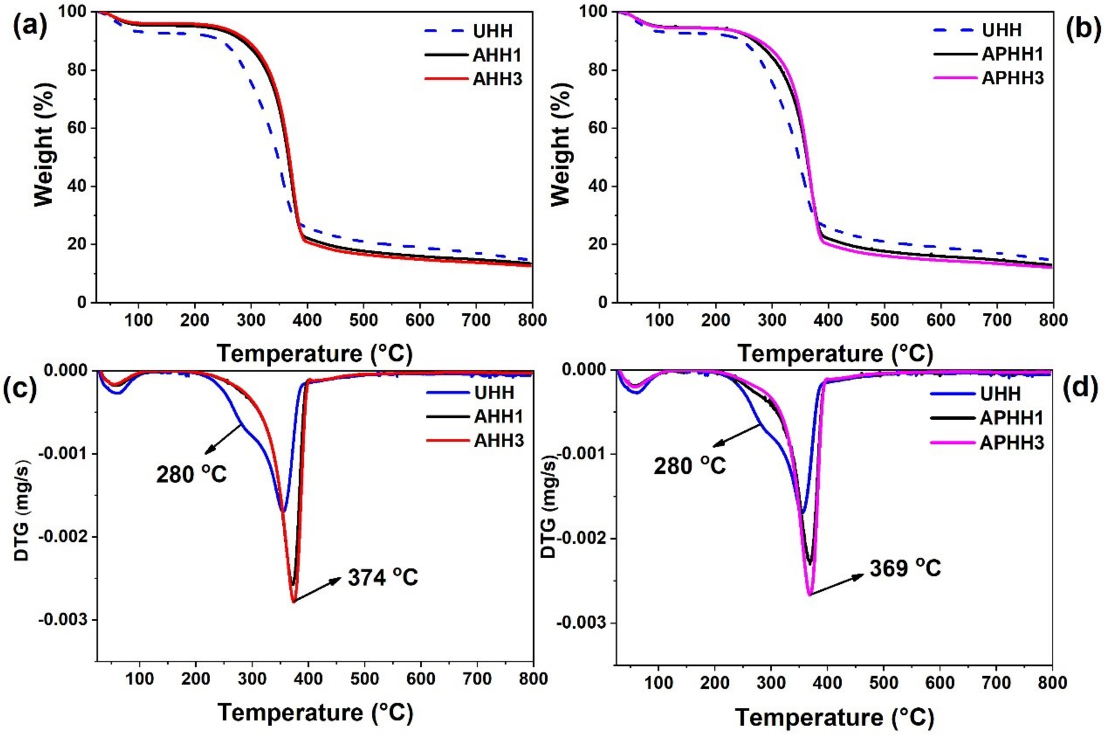

Figure 3.4. TGA thermograms of untreated, alkaline -treated (a), and alkaline/peroxide treated (b) hemp hurd powders, DTG thermograms corresponding to untreated, alkaline-treated (c), and alkaline/peroxide treated (d) hemp hurd powders

Table 3.3. T_{10} and T_{50} values of fiber samples extracted from TGA curves

Sample	T_{10} (°C)	T_{50} (°C)
UHH	246.5	347.1
AHH1	284.8	365.6
AHH3	294.0	368.4
APHH1	269.4	361.8
APHH3	278.6	363.3

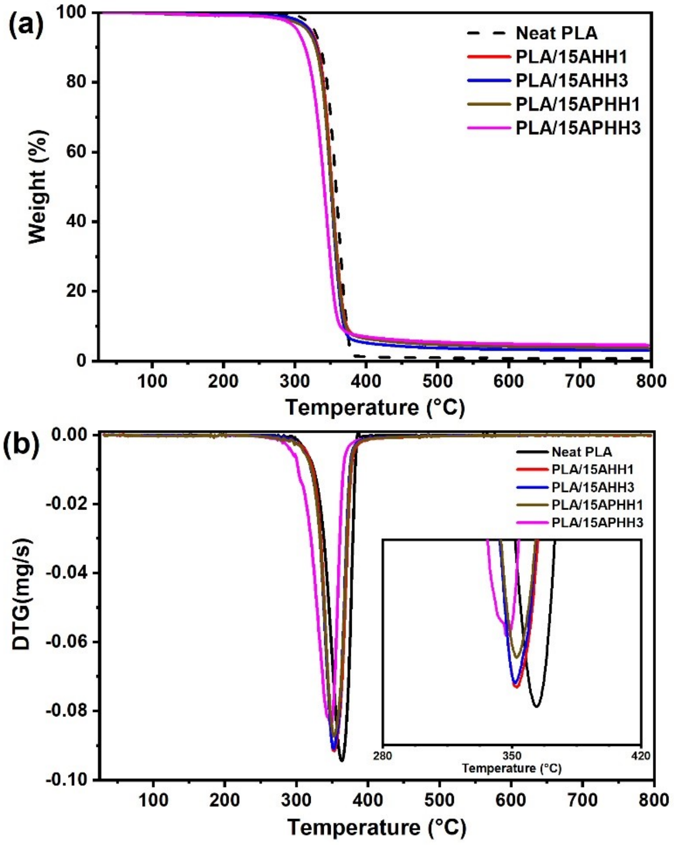

Figure 3.5. TGA (a) and DTG (b) thermograms of PLA and its biocomposites for 15 wt % filler loading

Table 3.4. Data obtained from TGA results of PLA and its biocomposites

Sample	T_i (°C)	T_f (°C)	T_{peak} (°C) at DTG	Char residue (%) at 799 °C
PLA	327.0	378.5	363.4	0.8
PLA/15AHH1	322.0	373.0	353.1	3.9
PLA/15AHH3	320.4	372.2	352.7	3.2
PLA/15APHH1	317.3	373.6	353.1	3.8
PLA/15APHH3	303.5	365.8	347.3	4.6

3.3.5. Thermal analysis of biocomposites

TGA and DTG thermograms of neat PLA and PLA/hemp hurd powder biocomposites containing 15 wt % of hemp hurd powder are presented in **Figure 3.5** (a) and (b). **Figure 3.5** (a) shows that all samples (neat PLA and PLA/hemp hurd powder biocomposites) exhibit a single-step degradation process. The initial decomposition temperature (T_i, corresponding to the temperature at which the sample mass has decreased by 5%), final decomposition temperature (T_f, corresponding to the temperature at which the sample mass has decreased by 90%), the temperature of maximum mass loss rate (T_{peak}, corresponding to the temperature of the peak in DTG thermogram), and the percentage of char residue for each sample were determined from TGA and DTG thermograms and are represented in **Table 3.4**. It was found that the addition of hemp hurd powder resulted in a reduction in both initial and final decomposition temperatures of the biocomposites as compared with neat PLA. This observation can be attributed to the fact that the thermal stability of both hemicellulose and cellulose is lower than the thermal stability of PLA [120]. Among the biocomposites, PLA/15AHH1 and PLA/15AHH3 exhibited T_i of 322 °C and 320.4 °C, respectively; indicating better thermal stability in terms of initial decomposition temperature compared to PLA/15APHH1 and PLA/15APHH3 samples, with T_i values of 317.3 °C and 303.5 °C, respectively. However, in terms of the final decomposition temperature, PLA/15APHH1 exhibited the highest T_f value of all biocomposites (373.6 °C). The PLA/15APHH3 biocomposite was found to be the least thermally stable sample, as it exhibited the lowest initial and final decomposition temperature. This observation could result from excessive delignification during the three-cycles of successive alkaline/peroxide treatment process, which may have degraded the structure of the hemp hurds [54].

Char residue (residual mass) at 799 °C for all of the biocomposites was found to be higher than that of PLA as presented in **Table 3.4**. This observation could be directly linked to the presence of hemp hurd powder in PLA matrix due to the fact that – unlike PLA – lignocellulosic fibers have a charring step in their thermal degradation process, where at the temperatures higher than lignin's degradation temperature range (200 °C – 500 °C) [121], both lignin and cellulose lead to the formation of char [122].

TGA and DTG curves corresponding to the composites containing 5 wt % and 15 wt % of treated hemp hurd powders are shown in Appendix A, **Figure S4**. The PLA/5AHH3 and PLA/15AHH1 samples exhibited better thermal stability considering the initial decomposition temperature with T_i values of 327 °C and 322 °C, respectively. PLA/5APHH3 and PLA/15APHH1 yielded higher final degradation temperature (T_f) of 376.1 °C and 373.6 °C, respectively. For all biocomposites, increasing the filler content resulted in a higher char residue at 799 °C. This char corresponds to the constituents of the hemp hurd powder (cellulose and lignin), which typically leave residue even at these high temperatures [123]. These observations are in accordance with the previously reported results by Singh et al., where they observed that increasing cellulose fibers content in PLA-based biocomposites resulted in higher char residue at 600 °C [94].

To ensure the processibility of PLA/hemp hurd powder biocomposites using melt-processing techniques, the thermal stability of hemp hurd powder within the processing temperature range is required. Considering the initial degradation temperature of biocomposites containing 15 wt % of treated hurd powder exceeds 250 °C, it can be inferred that melt processing of PLA/hemp hurd powder biocomposites at the melting temperature range of PLA (130 – 180 °C) [23] would not result in thermal degradation of the hemp hurd powder.

DSC thermograms corresponding to the second heating cycle of PLA and its biocomposites containing 15 wt % of hemp hurd powder are given in **Figure 3.6**, and the relevant data were extracted and are summarized in **Table 3.5**. It was found that incorporation of hemp hurd powder lowered the glass transition temperatures (T_g) of the biocomposites. This reduction was most prominent for the samples containing hemp hurd powder that underwent a single cycle of treatment (PLA/15APHH1 and PLA/15AHH1).

Each of the thermograms corresponding to the biocomposites exhibited peaks corresponding to a cold crystallization temperature (T_{cc}), and a melting temperature (T_m). However, a T_{cc} peak was not present in the thermogram of PLA, reflecting the amorphous nature of this material. Similarly, neat PLA exhibited only a small melting peak around 149.1 °C. For each of the biocomposites, only very small variations in melting temperatures were observed (ranging from 148.8 °C to 149.7 °C). Biocomposites containing three-cycle treated hemp hurd powder showed lower cold crystallization temperatures compared to the ones comprised of single-cycle treated hemp hurd powder. A reduction in cold crystallization temperature was observed previously for PLA upon the addition of increasing concentrations of pulp fibers, which were reasoned to act as heterogeneous nucleation sites [124]. Here, the results indicate that the heterogeneous nucleation of PLA occurred preferentially on hemp hurd powder that was exposed to a higher number of chemical treatment cycles.

PLA (without hemp hurd powder) exhibited the lowest crystallinity (1.3%), while the addition of treated hemp hurd powder resulted in a higher crystallinity. Biocomposites containing three-cycle treated hemp hurd powder yielded the highest crystallinity values of 18.7% and 18.5%, corresponding to PLA/15APHH3 and PLA/15AHH3, respectively. The increase in crystallinity of samples that occurred due to the incorporation of hemp hurd powder supports the idea that the treated hemp hurd powder acts as a nucleating agent in the PLA matrix, leading to the alignment of the PLA chains [89], [125]. DSC results of biocomposites for various filler proportions (5, 10, 15 wt %) are presented in Appendix A, **Figure S5**, for further clarification of the impact of filler loading on thermal properties of the biocomposites. **Figure S5** shows that increasing filler loading led to a further decrease in the glass transition temperature (T_g) of the biocomposites, where the lowest T_g was observed for the biocomposites with 15 wt % filler content. It was also observed that increasing filler loading increased the crystallinity of the biocomposites.

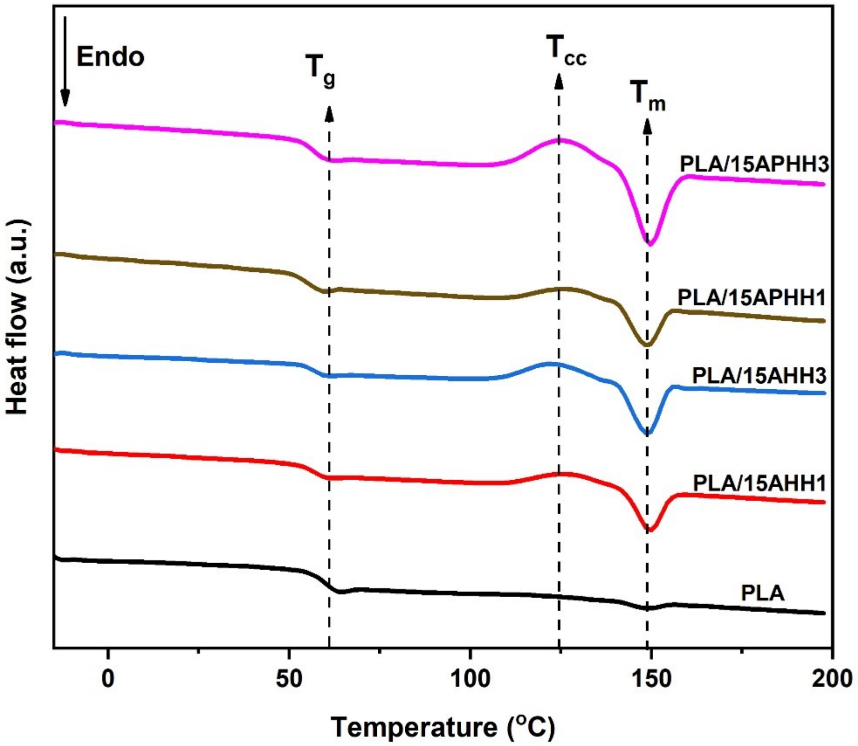

Figure 3.6. DSC thermograms of PLA and its biocomposites for 15 wt % filler loading

Table 3.5. DSC data corresponding to PLA and its biocomposites

Sample	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_m (J/g)	X_C (%)
PLA	60.4	-	149.1	1.28	1.3
PLA/15AHH1	56.1	125.3	149.6	10.62	13.0
PLA/15AHH3	56.4	122.3	148.9	15.13	18.5
PLA/15APHH1	55.0	125.7	148.8	9.11	11.2
PLA/15APHH3	56.5	124.8	149.7	15.28	18.7

3.3.6. Mechanical properties of biocomposites

Tensile properties of PLA and its biocomposites containing various proportions (5, 10, and 15 wt %) of untreated and treated hemp hurd powder were evaluated. To better understand the impact of hemp hurd powder on mechanical properties of biocomposites, samples were prepared with 15 wt % filler loading of untreated and treated hemp hurd powders, and the Young's modulus, tensile strength, and elongation at break of the samples are presented in **Figure 3.7**. Tensile results indicated that the addition of both untreated and treated hemp hurd powders to the PLA matrix resulted in a significant increase in Young's modulus, which is likely related to both the higher stiffness of hemp hurds and the increase in crystallinity of the material [126].

The addition of 15 wt % hemp hurd powder (prepared using the various treatment methods) resulted in a decrease in both elongation at break and tensile strength. The measured value of elongation at break for neat PLA was 5.7%, which was decreased to the range of 3.8% ~ 2.8% upon the addition of 15 wt % of hemp hurd powders. In the case of tensile strength, the value for neat PLA was determined to be 66.9 MPa. For PLA/15UHH sample, the obtained value of tensile strength was 50.7 MPa, corresponding to a 24% reduction in comparison to neat PLA. The reduction in tensile strength exhibited by biocomposites formed with untreated hemp hurd powder (UHH) with respect to PLA can be ascribed to inferior filler-matrix interaction caused by the high hydrophilicity of UHH. This powder contained hydrophilic components such as hemicellulose and lignin, which are incompatible with the hydrophobic PLA matrix.

Performing chemical treatments on the hemp hurd powder improved the filler-matrix compatibility to some extent, although the tensile strength values of the biocomposites were all lower than for neat PLA. Nonetheless, each of the biocomposites with treated hemp hurd powders showed higher tensile strength values compared to the PLA/15UHH sample. The chemical treatments increased the surface roughness of hemp hurd powder (as shown in SEM results), which is expected to improve the filler-matrix interfacial interaction. This can be achieved by enhancing mechanical interlocking mechanism between filler and polymer matrix [127], caused by the higher level of surface roughness, which can lead to higher friction once the filler is pulled out of the matrix. This mechanism can eventually promote the mechanical properties of the biocomposites reinforced with treated hemp hurd powders [114]. Among the biocomposites containing treated hurd powders, PLA/15APHH1 yielded the highest tensile strength with a value of 62.6 MPa, showing a 6.5% decrease compared to neat PLA and a 23% increase in comparison to the sample containing untreated hurd powder (PLA/15UHH). The efficient removal of hemicellulose, lignin, pectin, and wax from hemp hurd powder during alkaline/peroxide treatment led to an enhanced filler-matrix interaction in the case of PLA/APHH1 biocomposite.

In addition to exhibiting the highest tensile strength of the biocomposites, PLA/15APHH1 was determined to have the highest Young's modulus (2673.6 MPa), indicating an increase of 70% over neat PLA and a 10% increase as compared to PLA/15UHH. The tensile properties of the fabricated PLA/hemp hurd powder biocomposites are in agreement with the literature. B.A. Khan et al. evaluated the mechanical properties of PLA/hemp hurds biocomposites for various proportions of untreated hemp hurds (10, 20, and 30 wt %). They found that incorporation of hemp hurds decreased the tensile strength of the biocomposites in comparison to neat PLA, where increasing the filler content further decreased the tensile strength of the biocomposites. They attributed this observation to the inadequate fiber wetting which led to inferior fiber-matrix interaction [128]. Johari et al. also reported similar results regarding Young's modulus and strength in the case of PLA/cellulose fiber biocomposites [125]. They observed that the addition of cellulose fibers to PLA resulted in a decrease in tensile strength and ductility of fabricated biocomposites, while increasing the Young's modulus of biocomposites.

The tensile strength values of PLA/15AHH1 and PLA/15APHH1 samples were found to be comparable. However, it was noticed that the incorporation of three-cycle treated hemp hurd powder yielded lower tensile strength for the same filler loading in either case of alkaline and alkaline/peroxide-treated hemp hurd powder. This observation can be attributed to the excessive delignification and degradation of cellulose during third cycle of treatments, resulting in poor mechanical properties as stated in the work of Malenab et al., where they observed that increasing the immersion time of abaca fibers in NaOH solution resulted in lower tensile strength of fibers [54], [129]. Here, for 15 wt % filler content, biocomposites containing any kind of treated hemp hurd powders, regardless of the number of treatments, have been shown to have higher tensile strength than the PLA/15UHH biocomposite, indicating the impact of treatments on enhancing the mechanical properties – especially tensile strength – of the PLA/hemp hurd powder biocomposites.

The effect of filler loading on tensile properties of the biocomposites is shown in **Figure 3.8**, which shows the mechanical properties of biocomposites containing 0 wt %, 5 wt %, 10 wt %, and 15 wt % hemp hurd powder in PLA for each treatment type (untreated, alkaline-treated, and alkaline/peroxide-treated). **Figure 3.8** (a) shows that the addition of both untreated and treated hurd powders improved the Young's modulus, where increasing the filler content in most of the cases led to higher Young's modulus in biocomposites, indicating the stiffening effect of hemp hurds. Moreover, PLA/APHH1 was the only biocomposite containing treated hemp hurd powder that yielded higher Young's modulus than PLA/UHH in all of the filler contents stated in this study. In the case of the tensile strength (**Figure 3.8** (b)), it was found that the addition of 5 wt % or more of any type of hemp hurd powder to PLA reduced the tensile strength of the biocomposites.

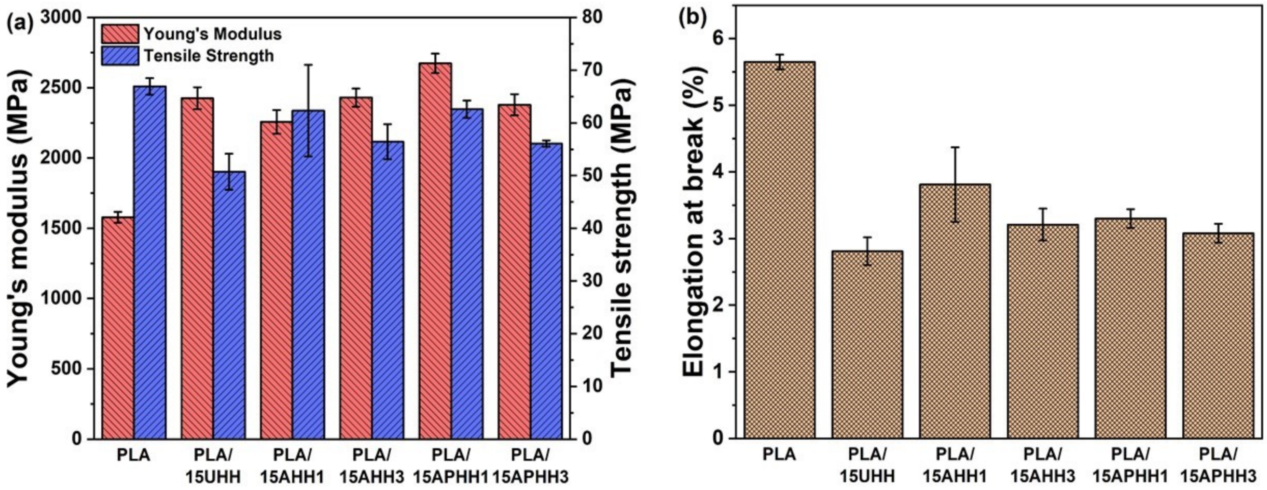

Figure 3.7. Mechanical properties of PLA and PLA/hemp hurd biocomposites with 15 wt % filler loading. (a) Young's modulus and tensile strength, (b) elongation at break (Note: average values and standard deviation of five independent measurements are shown).

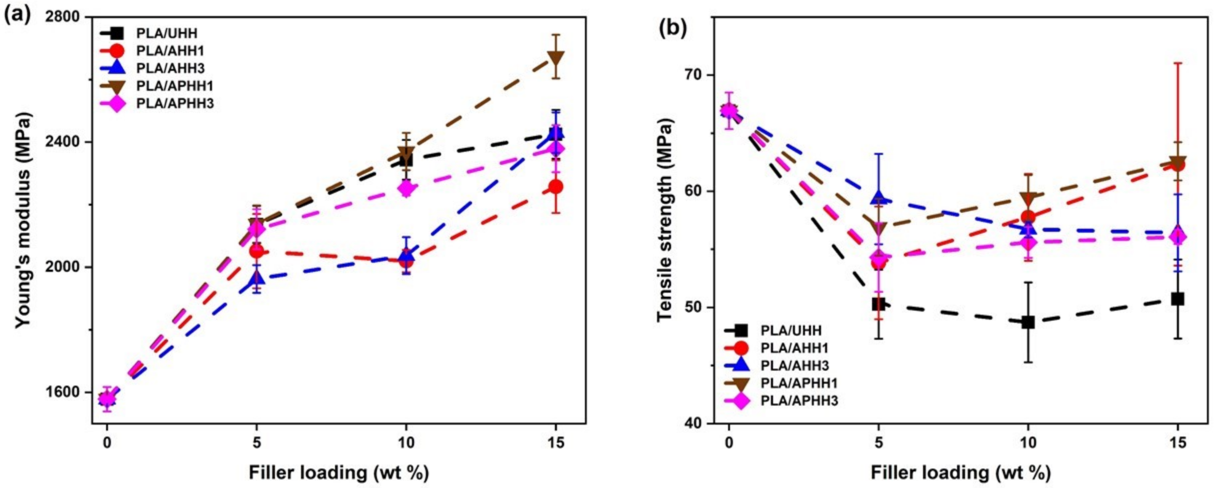

Figure 3.8. Young's modulus (a) and tensile strength (b) of PLA biocomposites for 5, 10, and 15 wt % filler loading (Note: average values and standard deviation of five independent measurements are shown) (Note: lines are drawn solely for the interest of clarity)

3.4. Conclusion

In this study, the mechanical and thermal properties of PLA/hemp hurd powder biocomposites were enhanced by performing one or three cycles of alkaline and alkaline/peroxide treatments on hemp hurd powder before compounding with PLA. Although the tensile strength of the biocomposites decreased in general compared to neat PLA, the tensile properties of biocomposites containing treated hemp hurd powder showed significant improvement compared to the samples comprised of untreated hemp hurd powder. Of all of the biocomposites, the one containing 15 wt % hemp hurd powder treated with a single cycle of alkaline/peroxide treatment (PLA/15APHH1) exhibited the best mechanical results in terms of tensile strength and Young’s modulus, exhibiting a 23% increase in tensile strength and 10% increase in Young’s modulus in comparison to the PLA/15UHH biocomposite, which is comprised of 15 wt % untreated hemp hurd powder. One drawback of the biocomposites is that the elongation at break – which is already relatively low for neat PLA – is further reduced through the addition of the filler. DSC results indicated that treated hemp hurd powder could act as nucleating agents leading to increased crystallinity of the PLA/hemp hurd powder biocomposites compared to PLA. Thermogravimetric analysis revealed that biocomposites containing treated hemp hurd powder exhibited proper thermal stability in the processing temperature range of PLA (130-180 °C) indicating the fact that this range of temperature does not pose any detrimental risk to the thermal stability of treated hemp hurds, and that these materials could subsequently be processed using thermal techniques such as injection molding, compression molding, and 3D printing without degrading the biocomposites. The results of this study suggest that PLA/hemp hurd powder biocomposites, as completely biodegradable and bio-based materials, may be a promising candidate for use in the packaging industry, particularly for applications requiring relatively stiff materials.

4. Plasticized PLA and PLA/hemp hurd powder

One of the main obstacles in large-scale applications of PLA, particularly for packaging purposes, is its inherent brittleness. A variety of commercial plasticizers are available in the market which is predominantly phthalate-based plasticizers such as Di(2-ethylhexyl) phthalate (DEHP). Using these plasticizers may have negative effects on the environment upon degradation when used in biopolymers. For instance, numerous studies have already reported the adverse effect of DEHP on human health due to the high migration level of this plasticizer [79]. To overcome the brittleness issue of biopolymers without compromising the biodegradability and biocompatibility of these materials, bio-based plasticizers which show low toxicity could be promising alternatives. Over the past few years, a variety of studies have examined the effect of vegetable oil-based plasticizers on various biopolymers. However, very few studies have reported the use of epoxidized canola oil (ECO) – which is obtained from low-value canola oil – as a bio-based plasticizer.

In this chapter, the materials and the preparation methods for plasticized biocomposites are introduced. The main materials used in this part of the study are PLA as polymer matrix, epoxidized canola oil (ECO) as bio-based plasticizer, and single-cycle alkaline/peroxide treated hemp hurd powder (APHH1, as described in Chapter 3) as reinforcing agent. The thermal and mechanical characterization used in Chapter 3 showed that the addition of single-cycle alkaline/peroxide treated hemp hurd powder (APHH1) to PLA matrix resulted in better mechanical and thermal properties as compared to the composites formed with other types of hemp hurd powder. However, the addition of hemp hurd powder to an already-brittle PLA matrix led to further embrittlement of the prepared biocomposites. To overcome this issue, the use of epoxidized canola oil (ECO) as a bioplasticizer is investigated. To explore the effect of ECO on the flexibility of the samples, a fixed composition of APHH1 (15 wt %) – based on the results obtained in Chapter 3 – is used. The thermal and mechanical properties of these materials are characterized by TGA, DSC, and tensile testing, and the results are presented. In addition, the stability/migration of the plasticizer is characterized.

4.1. Materials and methods

4.1.1. Materials

Poly(lactic acid) (PLA, nominal Mw: 390 kDa, grade 4043D pellets) was purchased from NatureWorks LLC, Minnetonka, MN, USA. Single-cycle alkaline/peroxide treated hemp hurd powder (APHH1) was used as the reinforcing agent and the preparation technique of APHH1 is described in Chapter 3, section 3.2.2.2. Epoxidized canola oil (ECO) was synthesized according to the method described by Mungroo et al. [130].

4.1.2. Preparation of plasticized samples

PLA and treated hemp hurd powder were dried at 70 °C overnight prior to use to remove moisture. The PLA/ECO and PLA/HH/ECO biocomposites were prepared using melt compounding technique in a co-rotating twin-screw extruder (HAAKE™ Minilab II micro compounder, Thermo Fisher Scientific, Waltham, MA, USA) at 160 °C with a rotor speed of 75 rpm. The extruded filaments were cooled to room temperature and then pelletized. Pellets were dried at 70 °C overnight prior to preparation of standard tensile test (ASTM D638) specimens using a hot-pressing machine (Model 4386, Carver Inc., Wabash, IN, USA) and a rectangular steel mold with dimensions of 70 mm × 80 mm. Samples were held under 2 MPa pressure at 180 °C for 5 min. Dumbbell-shaped specimens were cooled to room temperature and then stored in sealed plastic bags for further characterization. PLA/ECO and PLA/HH/ECO were prepared in various compositions (as shown in **Table 4.1**).

Table 4.1. Composition of plasticized samples

Sample	Filler	Filler content (wt %)	Plasticizer	Plasticizer content (wt %)
Neat PLA	-	-	-	-
PLA/5ECO	-	-	ECO	5
PLA/7.5ECO	-	-	ECO	7.5
PLA/10ECO	-	-	ECO	10
PLA/HH/5ECO	APHH1	15	ECO	5
PLA/HH/7.5ECO	APHH1	15	ECO	7.5
PLA/HH/10ECO	APHH1	15	ECO	10

4.2. Characterization

4.2.1. Thermogravimetric analysis (TGA)

The thermal stability of PLA/ECO and PLA/HH/ECO biocomposites was evaluated by TGA, using a TGA Q50 instrument (TA Instruments, New Castle, DE, USA). Samples, weighing ~10 mg each, were placed in aluminum pans and were heated from 25 °C to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere (40 mL/min) as the mass was monitored.

4.2.2. Differential scanning calorimetry (DSC)

The effect of ECO on the thermal properties of PLA and biocomposites were investigated using a differential scanning calorimeter (DSC Model 1, Mettler Toledo, Columbus, OH, USA). Samples of 8-10 mg were placed in sealed aluminum pans and then heated from -20 °C to 200 °C at a heating rate of 5 °C/min under nitrogen atmosphere. For each sample, the following heating/cooling cycle was used: in the first heating scan, samples were heated from -20 °C to 200 °C at a heating rate of 5 °C/min; samples were then cooled to -20 °C at a cooling rate of

5 °C/min; samples were then heated again to 200 °C at a heating rate of 5 °C/min. During these temperature cycles, heat flow transferred to/from the samples were measured. Glass transition temperatures (T_g), cold crystallization temperatures (T_{cc}), and melting temperatures (T_m) were obtained based on the data collected during the second heating cycle. The degree of crystallinity (X_c) of PLA and its biocomposites were calculated using the following equation:

$$X_c\,(\%) = \frac{\Delta H_m}{w \times \Delta H_m^0} \times 100$$

Where w is the weight fraction of PLA in the biocomposites, ΔH_m corresponds to the melting enthalpy of biocomposite, and ΔH_m^0 refers to melting enthalpy of pure crystalline PLA (96 J/g) [76].

4.2.3. Tensile testing

Tensile characteristics of PLA/ECO and PLA/HH/ECO biocomposites were determined in accordance with ASTM D638: *Standard Test Method for Tensile Properties of Plastics*, using a universal tensile testing machine (Instron 5943, Instron, Norwood, MA, USA) equipped with a 1 kN load cell. Tensile testing was carried out at a strain rate of 5 mm/min on a minimum of 5 samples of each type of biocomposite. The total length, gauge length, width, and thickness of the dumbbell shaped samples were 75 mm, 25 mm, 4 mm, and 2 mm, respectively. Tensile strength, Young's (tensile) modulus, and elongation at break were determined for each specimen, and average values and standard deviations are reported.

4.2.4. Plasticizer migration test

The tendency of the bio-based plasticizer (ECO) to migrate from the prepared biocomposites was evaluated according to ISO 177: *Plastics – Determination of migration of* *plasticizers*. For the purpose of this characterization, test specimens in the form of discs with 50 mm ± 1mm in diameter and 1.5 mm ± 0.1 mm in thickness were prepared using a hot-pressing machine and a steel mold using the procedure described in section 4.2.1. Polyethylene discs, 60 mm ± 1 mm in diameter and 2.0 mm ± 0.1 mm in thickness, were used as absorbent backing discs. Each test specimen was placed between two absorbent discs and the assembly forming a sandwich that was then placed between two glass plates (75 mm × 75 mm). In order to achieve equal distribution of pressure between the absorbent discs and the test specimen, a sheet of natural rubber was inserted between absorbent discs and glass plates. A standard weight (5 kg) was placed on the assembly of discs and plates (one weight per assembly of 6 sandwiches) and they were placed in an oven and maintained at a temperature of 50 °C. Three samples of each composition and test condition were tested and the average and standard deviation values are reported. The plasticizer migration level (%) was calculated using the following equation:

$$Plasticizer\ migration\ level\ (\%) = \frac{m_i - m_f}{m_i} \times 100$$

Where m_i and m_f are the initial and final mass of the test specimen, respectively. The final mass of the specimens were measured after test periods of 1 day, 2 days, and 7days.

4.3. Results and discussion

4.3.1. Thermal stability of plasticized samples

The TGA and derivative thermogravimetric (DTG) thermograms of PLA, PLA/ECO, and PLA/HH/ECO biocomposites are shown in **Figure 4.1** (a) and (b), respectively. As can be seen from this figure, all samples underwent a single-step decomposition process. Furthermore, the TGA thermograms of each biocomposite was shifted towards a lower temperature compared to the neat PLA sample, which suggests that the inclusion of ECO and hurd powder reduced the thermal stability of the prepared biocomposites. The initial degradation temperature (T_i), corresponding to the temperature at which 5% weight loss occurs, the maximum degradation temperature (T_{peak}), corresponding to the temperature of the peak in DTG thermograms, and T_{50}, the temperature at which 50% weight loss occurs, were extracted from TGA and DTG thermograms and the results are summarized in **Table 4.2**. Neat PLA showed a T_i value of 324.9 °C and T_{peak} value of 369.1 °C. When only ECO was added, only small changes in T_i and T_{peak} were observed for the two lower concentrations (5 wt % and 7.5 wt %). However, when the content of ECO was increased to 10 wt % (PLA/10ECO), noticeable reductions in initial and maximum degradation temperatures occurred, as T_i and T_{peak} dropped to 310.8 °C and 359.3 °C, respectively. It can be inferred that addition of more than 7.5 wt % ECO to PLA resulted in a saturated composition, which adversely impacted the thermal stability of the PLA/ECO biocomposite. Similar results were reported by A. Orue et al. for PLA plasticized with 10 wt % epoxidized linseed oil (ELO) and epoxidized soybean oil (ESBO) [84]. Contrary to our observations, some reports in the literature indicate that addition of epoxidized vegetable oil can actually improve the thermal stability of PLA-based composites. For instance, L. Quiles-Carrillo et al. evaluated the thermal stability of PLA composites plasticized with various compositions (2.5, 5, 7.5, and 10 wt %) of epoxidized soybean oil [87]. They reported that for all of the above-mentioned compositions, TGA thermograms moved toward higher temperatures, indicating that incorporation of epoxidized soybean oil improved the thermal stability of the samples. This was not the case here.

Further decreases in the thermal stability of the samples was observed with addition of single-cycle alkaline/peroxide treated hemp hurd powder to form PLA/HH/ECO composites. In Chapter 3 the T_i and T_{peak} of PLA/HH samples containing 15 wt % hemp hurd subjected to the same treatment, without ECO, were found to be 317.3 °C and 353.1 °C, respectively. This can be attributed to the lower thermal stability of the lignocellulosic fibers in comparison to PLA. From the TGA thermograms of treated hemp hurd powders shown in **Figure 3.4** (Chapter 3), the T_i (i.e. the temperature at which 5% weight loss occurs) value for single-cycle alkaline/peroxide treated hemp hurd powder was found to be 99.8 °C, which is significantly lower than that of neat PLA. The addition of plasticizer (ECO) further shifted the initial degradation temperature of the composites to lower temperatures, where PLA/HH/5ECO showed the lowest T_i value (305.9 °C).

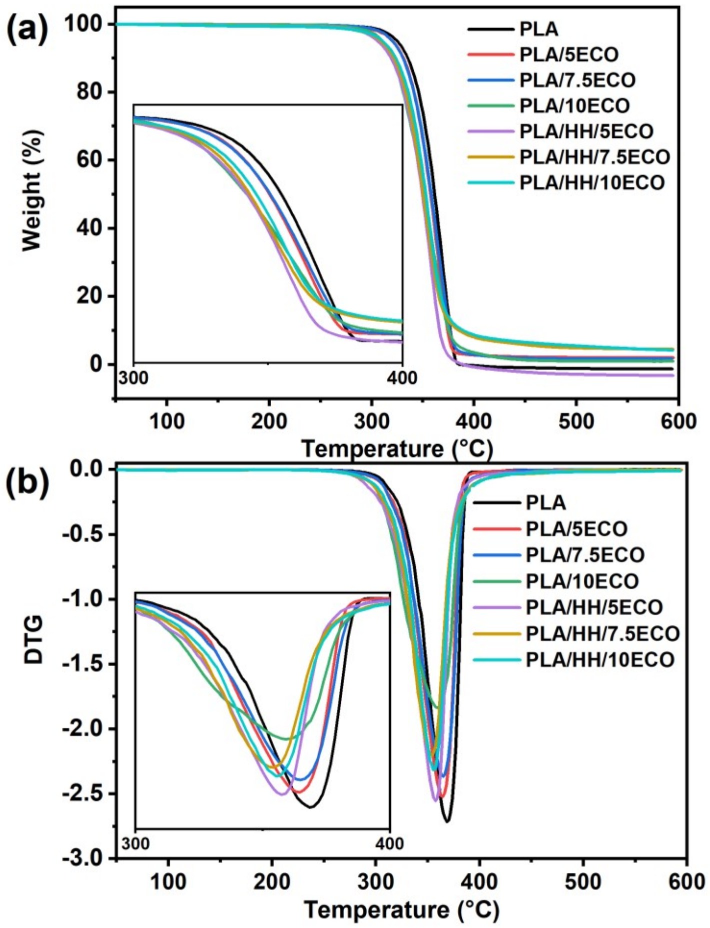

Figure 4.1. TGA and DTG results of plasticized samples. Inset images depict the region from 300 °C to 400 °C for each image.

Table 4.2. Data obtained from TGA and DTG results of plasticized samples

Samples	T_i (°C)	T_{peak} (°C)	T_{50} (°C)
PLA	324.9	369.1	361.5
PLA/5ECO	320.5	364.0	357.4
PLA/7.5ECO	320. 3	364.7	358.1
PLA/10ECO	310.8	359.3	351.2
APHH1*	99.8	368.7	361.8
PLA/APHH1**	317.3	353.1	351.0
PLA/HH/5ECO	305.9	357.8	349.6
PLA/HH/7.5ECO	308.9	353.7	350.5
PLA/HH/10ECO	311.0	356.1	352.7

* This data is obtained from **Figure 3.4** in Chapter 3.

** This data is obtained from **Figure 3.5** in Chapter 3.

4.3.2. Thermal properties of plasticized samples

DSC thermograms of plasticized samples obtained from second heating cycle are shown in **Figure 4.2**, and relevant data are summarized in **Table 4.3**. Neat PLA showed a glass transition temperature at 60.4 °C. As can be seen in **Table 4.3**, the addition of ECO reduced the glass transition temperature (T_g) of the PLA/ECO and PLA/HH/ECO biocomposites compared to neat PLA, where higher ECO content led to lower T_g. This observation could be directly related to the plasticizing effect of ECO on PLA. From a physical perspective, ECO enters into PLA polymer chains which leads to an increase in the free volume, facilitating the polymer chain motions at lower temperatures. None of the samples exhibited exothermic peak corresponding to cold crystallization process. This means that all of the samples had sufficient time during the cooling cycle for crystallization to occur. Endothermic peaks indicative of the melting process can be seen for all samples around 150°C. In semi-crystalline polymers, this transition occurs due to the melting the crystallites, and it was observed that addition of ECO as plasticizer and hemp hurd powder as filler did not significantly alter T_m. It can be inferred that neither of the additives affected the crystallite structure, therefore, no significant change in T_m was observed.

PLA is a semi-crystalline polymer which showed a crystallinity of 1.3% in this study. Addition of ECO as plasticizer slightly reduced the crystallinity of the PLA/ECO samples for 7.5 wt % and 10 wt % compositions. In our previous study, it was shown that alkaline/peroxide treated hemp hurd powder can act as nucleating agent, increasing the crystallinity of PLA-based biocomposites (11.5 % for PLA/APHH1). However, the results shown in **Table 4.3** show that addition of both ECO and HH to form PLA/HH/ECO biocomposites hinders the nucleation process, hence the crystallinity of the samples containing both hemp hurd powder and ECO increases only slightly compared to neat PLA (from 1.3% to 3%). This observation can be possibly attributed to phase separation of plasticizer and polymer matrix. This is contrary to our expectation that the addition of ECO (as a plasticizer) would improve the crystallinity of the samples by increasing chain mobility, which facilitating the rearrangement of polymer chains into more ordered structure [86], [131].

The DSC results reported in this study are in agreement with literature. A. Orue et al. observed that addition of various proportions (5, 10, 20 wt %) of epoxidized linseed oil (ELO) and epoxidized soybean oil (ESBO) did not substantially increase the crystallinity of PLA-based composites [84]. They also investigated the effect of plasticizer on the crystallinity of PLA/sisal fiber composites, and their results show that addition of ELO and ESBO only slightly increased the crystallinity of the samples compared to the composites without plasticizer. Nevertheless, it is reported in some studies that addition of epoxidized plant-based plasticizer to PLA efficiently improved the crystallinity. For instance, A. Carbonell-Verdu et al. reported that addition of 2.5 wt % and 10 wt % of epoxidized cottonseed oil (ECSO) to PLA (crystallinity of 20.5%) yielded PLA/ECSO samples with crystallinity of 31.3% and 32.3% [14].

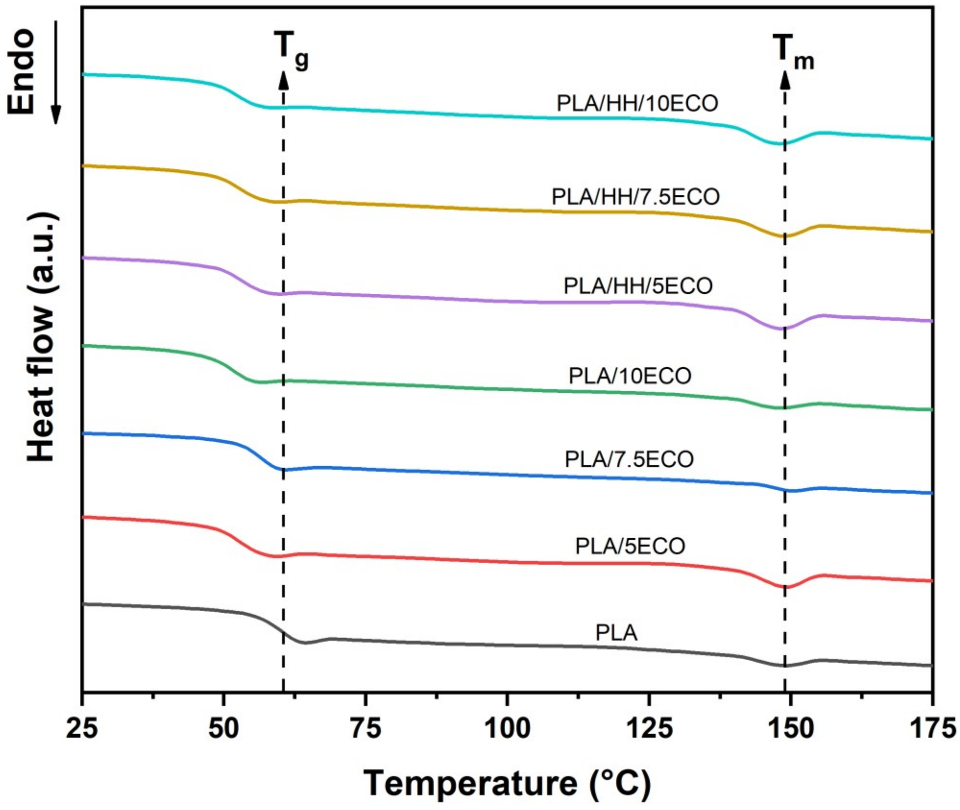

Figure 4.2. DSC thermograms of plasticized PLA and the biocomposites

Table 4.3. Data obtained from DSC thermograms of plasticized samples

Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)	Crystallinity (%)
PLA	60.4	149.1	1.28	1.3
PLA/5ECO	53.3	149.1	1.87	2.1
PLA/7.5ECO	53.2	150.3	0.45	0.6
PLA/10ECO	51.5	148.2	0.82	1.0
PLA/APHH1*	55.0	148.8	9.11	11.2
PLA/HH/5ECO	53.1	148.5	2.29	3.0
PLA/HH/7.5ECO	53.1	148.9	1.87	2.5
PLA/HH/10ECO	52.8	148.2	2.06	2.9

* This data is obtained from **Table 3.5** in Chapter 3.

4.3.3. Tensile properties

Tensile properties of PLA, PLA/ECO, and PLA/HH/ECO biocomposites containing different proportions of ECO (5 wt %, 7.5 wt %, and 10 wt %) were evaluated, and the results including the Young's modulus, tensile strength, and elongation at break were shown in **Figure 4.3** (a) – (d) (Stress – strain curves are shown in Appendix A, **Figure S6**). Neat PLA showed an elongation at break and tensile strength of 5.7% and 66.9 MPa, respectively. As it can be observed in **Figure 4.3** (a), the addition of ECO to PLA led to a significant improvement in elongation at break of PLA/ECO samples. The elongation at break was highly sensitive to the concentration of ECO: while the addition of 5 wt % ECO increased the elongation at break to 21.7%, the addition of 7.5 wt % ECO led to a remarkable improvement in elongation (104.4%), which is a 1732% increase compared to neat PLA. This observation clearly shows the plasticizing effect of ECO, which enhanced PLA polymer chains mobility by reducing the intermolecular forces leading to improved ductility of the PLA/ECO biocomposites. On the other hand, it was observed that further increase in ECO content to 10 wt %, decreased the elongation at break to 53.8%, which is still considerably higher compared to neat PLA. It can be inferred that 7.5 wt % ECO was the optimum concentration of ECO as plasticizer in PLA matrix, above which mechanical properties in terms of elongation at break start to deteriorate due to possible phase separation, as reported by previous studies [132]. It can be seen in **Figure 4.3** (b) that addition of ECO to PLA matrix led to a slight increase in Young's modulus. It was also observed that incorporating ECO into PLA matrix resulted in a decrease in tensile strength of the samples due to the plasticizing effect of ECO leading to reduced polymer-polymer interaction, where PLA/10ECO showed the lowest tensile strength value of 41.2 MPa, which represents a 38.4% decrease compared to neat PLA. Similar results were reported by D. Garcia-Garcia et al., where they observed that increasing epoxidized karanja oil (EKO) content beyond 5 wt % not only decreased the tensile strength of the PLA-based composites compared to neat PLA sample, but also resulted in decreased elongation at break as compared to other plasticized samples with lower concentration of EKO (1%, 2.5%, and 5%) [133].

The elongation at break results of PLA/HH/ECO biocomposites for various proportions of plasticizer are shown in **Figure 4.3** (c). It is evident that incorporation of 15 wt % alkaline/peroxide treated hemp hurd powder significantly increased the brittleness of the materials due to higher stiffness of the hemp hurd powder. The addition of 5 wt % and 7.5 wt % of ECO did not provide sufficient plasticizing effect to compensate for the brittleness of the samples imposed by hemp hurd powder. However, increasing the ECO content to 10 wt % improved the elongation at break of the biocomposite to a value of 6.2%, which represents a 10% increase in comparison to neat

PLA. This concentration of ECO improved the filler-matrix interfacial interaction, resulting in a proper stress transfer between PLA matrix and hemp hurd powder.

Tensile strength and tensile modulus results of PLA/HH/ECO biocomposites are presented in **Figure 4.3** (d). It can be seen that addition of hemp hurd powder improved the tensile modulus of the samples due to the stiffness of hemp hurd powder. It was reported in our previous study that incorporation of 15 wt % alkaline/peroxide treated hemp hurd powder in PLA improved the tensile modulus of the composite up to a value of 2673.6 MPa. However, in the ternary system of PLA/HH/ECO, the addition of ECO as plasticizer hindered the stiffness enhancement process to some extent; therefore, the tensile modulus results of PLA/HH/ECO biocomposites are not as high as PLA/hemp hurd powder biocomposites. The highest tensile modulus in PLA/HH/ECO ternary system was observed for the composite containing 7.5 wt % ECO with a value of 1952.1 MPa, which is a 24% increase compared to neat PLA. In the case of ternary system of PLA/HH/ECO, higher ECO content resulted in lower tensile strength of the samples, which can be attributed to the plasticizing effect of ECO. These observations are in accordance with the results reported in the literature. For instance, Balart et al. investigated the effect of epoxidized linseed oil (ELO) on the tensile properties of PLA reinforced with 20 wt % hazelnut shell flour (HSF) composites in order to reduce the fragility of the PLA/HSF sample by using a bio-based plasticizer [86] . Their results indicated that addition of ELO decreased the mechanical properties in terms of tensile strength and tensile modulus, with higher amounts of ELO resulting in lower values of each of these properties. They reported that sample containing the highest concentration of ELO (22.5 wt %) exhibited the lowest tensile strength and tensile modulus with values of 15.3 MPa and 590 MPa, respectively, while the control sample (PLA reinforced with 20 wt % HSF) showed values of 45 MPa and 1019 MPa, respectively.

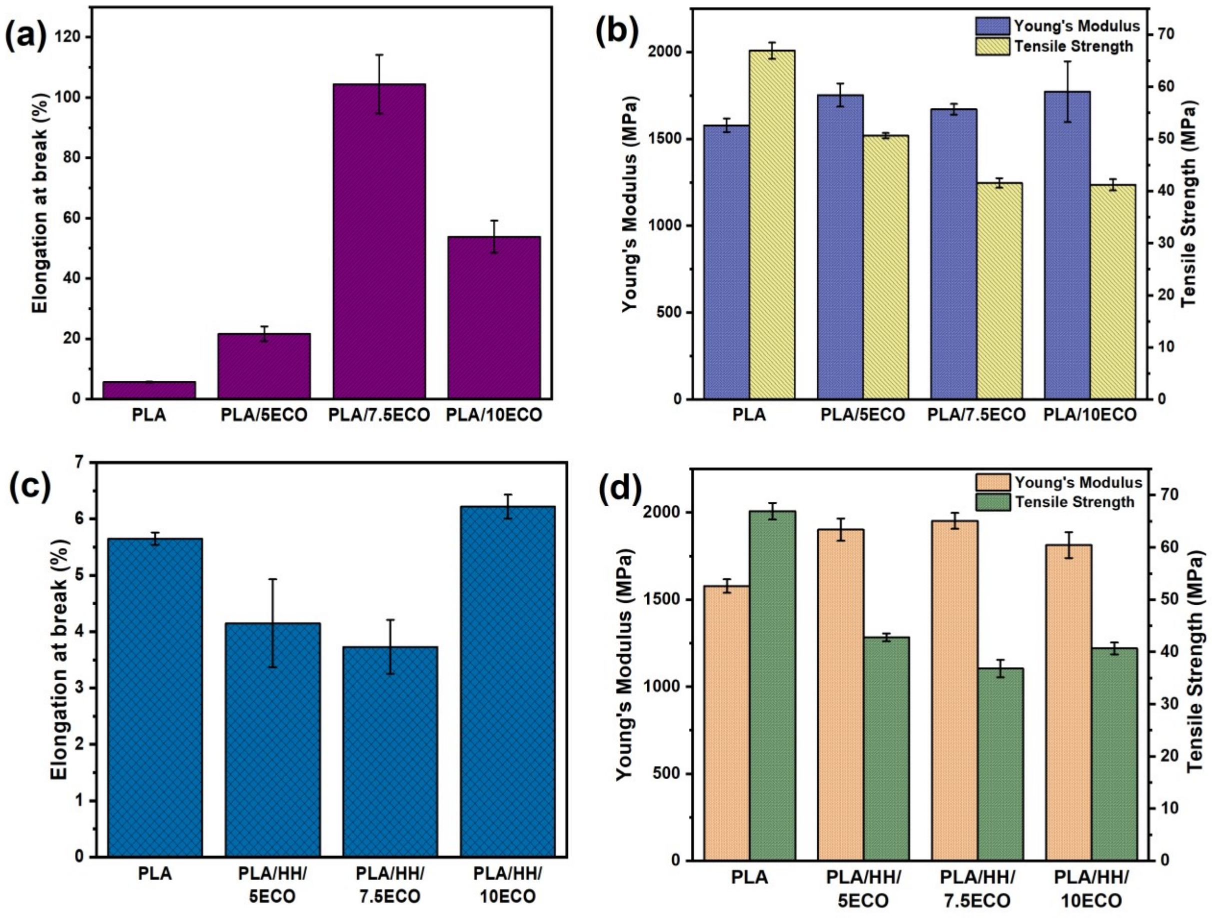

Figure 4.3. Mechanical properties of plasticized PLA and plasticized PLA/hemp hurd powder biocomposites. (a) Elongation at break, (b) Young's modulus and tensile strength for plasticized PLA samples. (c) Elongation at break, (d) Young's modulus and tensile strength for plasticized PLA/hemp hurd powder. (Note: average values and standard deviation of five independent measurements are shown)

4.3.4. Plasticizer migration level

The plasticizer migration level was determined for PLA/ECO and PLA/HH/ECO biocomposites using the ISO 177 standard and the corresponding results are shown in **Figure 4.4**. Over the 7 days of study, the plasticizer migration ranged from around 0.05 % to 0.35 % of the total sample weight. It can be seen that the plasticizer migration level increases with time for all samples, and therefore the maximum migration level was observed at 7 days. **Figure 4.4** also shows that PLA/ECO samples exhibit lower plasticizer migration levels compared to

PLA/HH/ECO biocomposites at each time point for a given concentration of ECO. It can be seen that PLA/ECO and PLA/HH/ECO biocomposites with the highest ECO content exhibited the lowest plasticizer migration levels at each time point. In the case of PLA/ECO biocomposites, this observation can be in part attributed to the improved compatibility between ECO and PLA due to the presence of epoxy groups in ECO structure, which led to a strong interaction with the hydroxyl groups of PLA. The possible explanation for higher plasticizer migration level in PLA/5ECO sample compared to PLA/7.5ECO and PLA/10ECO could be due to insufficient amount of ECO in the blend, resulting in poorer PLA – ECO interactions which facilitates the migration of the plasticizer. Similarly, the lower migration levels in PLA/7.5ECO and PLA/10ECO can be attributed to stronger interactions between PLA matrix and ECO. The impact of this improved compatibility between ECO and PLA with higher ECO content was observed in tensile testing results, where PLA samples plasticized with 7.5 wt % and 10 wt % ECO showed higher elongation at break values compared to PLA/5ECO sample. Overall, the plasticizer migration level in PLA/ECO biocomposites for all concentrations of ECO (5 wt %, 7.5 wt %, and 10 wt %) was less than 0.15% in all testing periods which indicates a very low plasticizer migration level. Similar results regarding the migration of epoxidized vegetable oil-based plasticizers have been reported in the literature. For instance, Carbonell-Verdu et al. investigated the plasticizing effect of epoxidized cottonseed oil (ECSO) on PLA [14]. They reported that the maximum plasticizer migration level was less than 0.12% for various concentrations of ECSO (up to 10 wt %) which is considered as a very low migration level. They attributed this phenomenon to the good compatibility between plasticizer and PLA matrix due to the strong interaction of epoxy groups in ECSO with hydroxyl groups present in PLA.

For all concentration of ECO, PLA/HH/ECO biocomposites showed higher plasticizer migration level compared to the PLA/ECO biocomposites. It can be inferred that the presence of hemp hurd powder adversely impacted the miscibility of ECO with PLA matrix, resulting in possible phase separation of plasticizer and thus higher level of migration. For PLA/HH/ECO samples, the plasticizer migration level decreased as the ECO content increased in the samples, where the lowest migration level was observed for PLA/HH/10ECO samples in all testing periods. This phenomenon could be attributed to the fact that low concentration of ECO (less than 7.5 wt %) does not sufficiently wet the hemp hurd surface, so that the strong HH – PLA interactions could not be achieved. As a result, a possible phase separation could occur at low concentrations of ECO leading to higher migration level. However, for relatively higher concentration (7.5 wt % and 10 wt %), ECO could act as a coupling agent [86] between the hemp hurd powder and plasticized PLA matrix leading to stronger HH – PLA interactions and hence lower plasticizer migration level. Although the addition of hemp hurd powder led to higher plasticizer migration level in the PLA/HH/ECO ternary system as compared to PLA/ECO, the maximum plasticizer migration level for PLA/HH/ECO samples did not exceed 0.35% - which is still a very low migration level – for any concentrations of ECO.

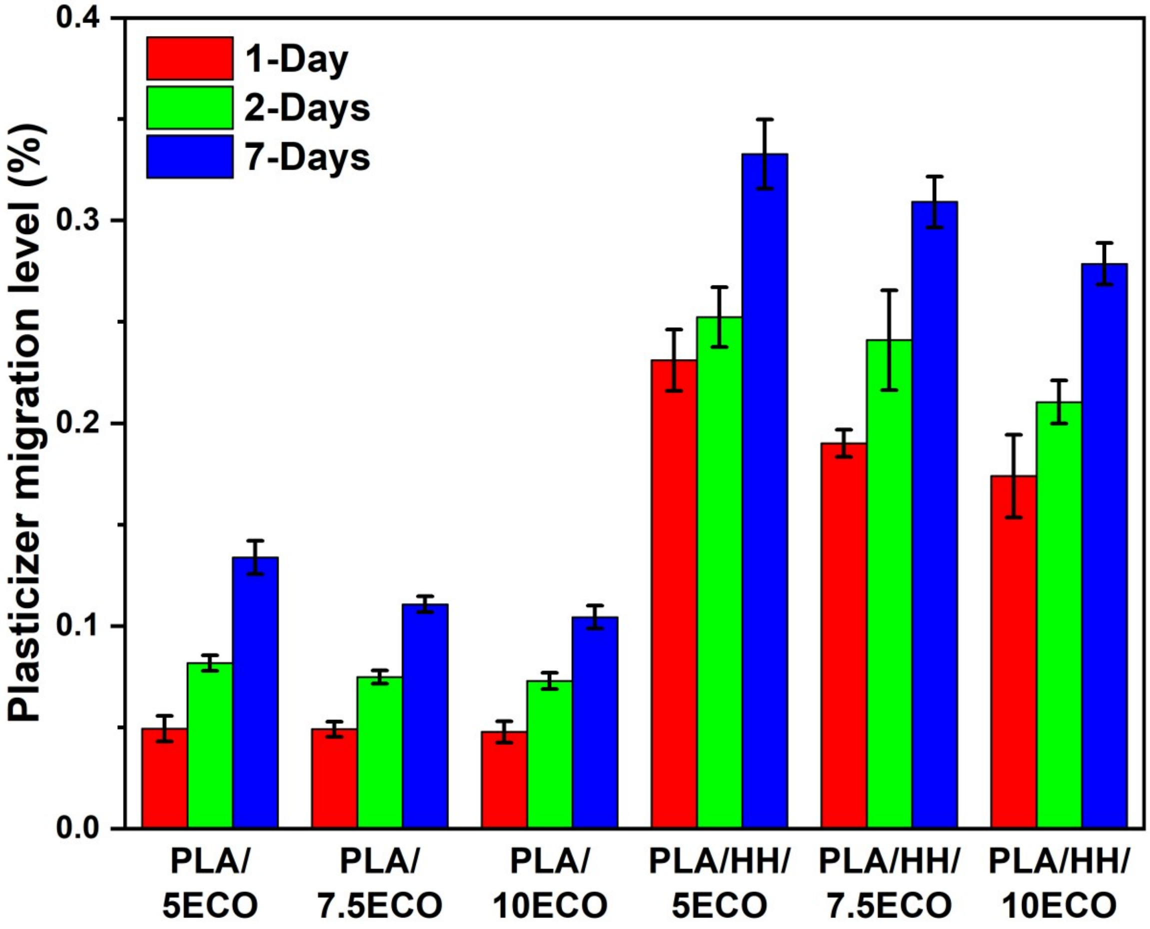

Figure 4.4. Plasticizer migration level for plasticized samples in 1-day, 2-days, and 7-days test period.

4.4. Conclusion and summary

In this section, epoxidized canola oil (ECO) has been proposed as a novel bio-based plasticizer for reducing the brittleness of PLA and PLA-based composites. The plasticizing effect of ECO was evaluated on neat PLA and PLA reinforced with 15 wt % single-cycle alkaline/peroxide treated hemp hurd powder using various concentrations of ECO (5%, 7.5%, and 10%). The plasticized samples were prepared using extrusion (for melt-mixing) followed by hot-pressing technique. The TGA analysis indicate that the addition of ECO (up to 7.5 wt %) to PLA matrix, did not have a significant effect on the thermal stability of the samples. However, PLA containing 10 wt % ECO and all of the plasticized PLA/hemp hurd powder samples experienced a moderate decrease (13.9 °C – 19 °C) in the initial degradation temperature, indicating decreased thermal stability of the plasticized samples.

DSC data was collected to study the thermal properties of the plasticized samples, while also determining the plasticizing effect of ECO in terms of decrease in the glass transition temperature (T_s). The DSC results showed that all of the plasticized samples underwent a remarkable reduction in T_g, indicating the plasticizing effect of ECO. It was also determined that the addition of ECO did not have a significant effect on the crystallinity of plasticized samples.

The plasticizing effect of ECO on PLA and PLA/hemp hurd powder biocomposites is evident from tensile testing results. With the addition of ECO to PLA matrix, a significant increase in elongation at break was observed for all of the ECO concentrations, while the sample plasticized with 7.5 wt % ECO showed an elongation at break value of 104.4%, which indicates a 1732% increase as compared to neat PLA. Using higher concentrations of ECO (10 wt %) adversely affected the elongation at break – although the elongation at break of PLA/10ECO was still higher than that of neat PLA – partly due to the phase separation of plasticizer. Nevertheless, using 7.5 wt % and 10 wt % ECO in PLA resulted in elongation at break values of higher than 50%, which was the targeted value for using ECO as plasticizer in this study. In the case of the ternary PLA/HH/ECO system, the addition of lower contents of ECO (5% and 7.5%) did not significantly improve the elongation at break due to the insufficient content of plasticizer to overcome the brittleness imposed by hemp hurd powder. However, using a higher concentration of ECO (10 wt %) provided proper stress transfer between PLA matrix and hemp hurd powder, leading to an elongation at break value of 6.2%, which is 10% higher compared to neat PLA. All of the plasticized samples experienced decrease in tensile strength due to the plasticizing effect of ECO.

In the case of PLA/HH/ECO ternary system, the addition of hemp hurd powder, only improved the tensile modulus of the plasticized samples with no significant effect on the tensile strength of PLA/HH/ECO samples compared to PLA/ECO samples with the same plasticizer content.

The maximum plasticizer migration level in PLA/ECO and PLA/HH/ECO biocomposites was found to be less than 0.15% and 0.35%, respectively. The very low migration level in PLA/ECO samples was mainly due to the presence of epoxide groups in the structure of ECO which contributed to stronger PLA – ECO interactions. In the case of PLA/HH/ECO ternary system, the low migration level can be attributed to the presence of ECO which improved the HH – PLA interactions.

The results of this study indicates that epoxidized canola oil (ECO) can be used as a bio-based plasticizer to reduce the fragility and brittleness of PLA and PLA-based materials. The mechanical properties of PLA/ECO biocomposites suggest that this material could be a promising alternative to replace the petroleum-based polymers in packaging applications which require flexible materials.

5. Conclusions and future work

5.1. Conclusions

In this work, hemp hurds and ECO were introduced as bio-based additives for PLA matrix to improve the thermal and mechanical properties while reducing the overall cost of PLA-based materials. Alberta is one of the main growers of canola plant – from which canola oil is extracted – and hemp plant in Canada. Finding proper utilization for agricultural waste produced by companies working on hemp and canola is environmentally and economically beneficial for the companies and government. . In addition, two industrial-scalable melt-processing techniques (i.e. extrusion and hot-pressing) were used to fabricate PLA-based composite specimens for characterizations. In general, this study explored the potential of PLA-based biocomposites to be utilized as stiff or flexible materials in industrial applications such as packaging by tailoring the composition and type of the additives.

Hemp hurds were used as inexpensive bio-based reinforcing filler in PLA matrix to both to improve the mechanical properties – in terms of tensile modulus – and reduce the overall cost of the material in potential large-scale applications. One or three cycles of alkaline and alkaline/peroxide treatments were performed on hemp hurd powder before compounding with PLA matrix to improve the filler-matrix interaction and hence the mechanical properties. Although the tensile strength of biocomposites decreased in general compared to neat PLA, the tensile strength of all the biocomposites containing treated hemp hurd powder showed a significant improvement in comparison to the samples formed of untreated hemp hurd powder. Moreover, all of the biocomposites containing hemp hurd powder, either treated or untreated, showed higher Young's modulus values compared to neat PLA due to the higher stiffness of hemp hurds. Of all of the samples, the one comprised of 15 wt % single cycle alkaline/peroxide treated hemp hurd powder (PLA/15APHH1) showed the best mechanical results in terms of tensile strength, Young's modulus, and elongation at break in comparison to the PLA/15UHH sample, which is formed of 15 wt % untreated hemp hurd powder. The results revealed that all of the samples containing treated hemp hurd powder showed proper thermal stability in the melt-processing temperature range of PLA (130-180 °C), indicating that the treated hemp hurd powder can be used in melt-processing techniques without undergoing thermal degradation. The results suggest that PLA/hemp hurds biocomposites can be used as a bio-based and biodegradable alternative to the conventional plastics in packaging applications, in particular for applications requiring relatively stiff materials.

The bio-based plasticizer, ECO, was mixed with neat PLA matrix and PLA/hemp hurds biocomposites to investigate the plasticization effect of ECO. With the incorporation of ECO in neat PLA, significant improvement in elongation at break of the samples was observed, where the sample containing 7.5 wt % ECO (PLA/7.5ECO) showed the highest elongation at break with a value of 104.4%, which indicates a 1732% increase in elongation at break compared to neat PLA. However, addition of ECO to PLA matrix led to a decrease in tensile strength of the samples due to the plasticizing effect of ECO. In the case of PLA/HH/ECO ternary system, containing 15 wt % single cycle alkaline/peroxide treated hem hurd powder (APHH1), only addition of 10 wt % of ECO resulted in a significant improvement in the elongation at break compared to neat PLA. Plasticizer migration level was tested for all of the samples plasticized with ECO. For all of the plasticized samples (with and without hemp hurd powder), the plasticizer migration level was below 0.35% which is a very low migration level. These results indicate that the plasticized PLA and PLA/hemp hurd powder biocomposites could potentially be utilized in packaging applications, particularly for the purposes requiring flexible and ductile materials.

5.2. Future work and recommendations

5.2.1. Thermal degradation of PLA

It is reported that thermal degradation can significantly compromise the mechanical properties, particularly the tensile strength, of polymers [134]. PLA, like many other aliphatic polyesters, is prone to thermal degradation during the melt-processing techniques at elevated temperatures [135]. Therefore, suitable characterizations are required to determine the rate and extent of thermal degradation that occurs to PLA samples during the melt-processing as well as by incorporation of additives (i.e. hemp hurds and ECO). One effective method is using gel permeation chromatography technique (GPC) to analyze the molecular weight distribution of the polymer and compare the initial value with the values obtained for samples after each melt-processing technique. Generally, the thermal degradation process of a polymer is accompanied by a drastic reduction in molecular weight (both weight average, M_w, and number average, M_n) of the samples. For instance, Pilla et al. investigated the thermal degradation of PLA and PLA reinforced with recycled wood fiber (RWF) using GPC method [136]. They observed that PLA reinforced with 20 wt % RWF underwent a 29% reduction in M_n compared to the neat PLA. They inferred that residual moisture in RWF could have initiated the hydrolysis process of PLA leading to molecular degradation.

5.2.2. Improving filler-matrix interaction

In the completed study, chemical treatments (alkaline and alkaline/peroxide) were performed to achieve a proper filler-matrix interaction in the case of PLA/hemp hurds biocomposites. These treatments were effective in partial removal of hemicellulose and lignin from hemp hurds. However, the interaction between treated hemp hurd powder and PLA matrix was not strong enough to result in an improvement in the tensile strength compared to neat PLA. Therefore, other approaches can be investigated to enhance the filler-matrix interaction. Incorporation of a compatibilizer could be a good starting point since some studies have reported improved mechanical properties in the natural fiber-reinforced polymer composites containing compatibilizer. For example, Yu et al. investigated the effect of using maleic anhydride (MA) as compatibilizer on the properties of PLA/ramie fiber composites [74]. They observed that incorporation of 3 wt % MA to PLA matrix prior to compounding with ramie fibers, improved the tensile strength and elongation at break of the samples compared to the PLA/ramie fiber composites without compatibilizer.

5.2.3. Barrier properties of prepared biocomposites

The barrier properties of materials is an important factor in selecting the food packaging materials. The barrier properties including the permeability to oxygen, carbon dioxide, and water vapor have fundamental impact on the quality of the packaged food. The barrier properties of the prepared biocomposites in this study should be evaluated in order to determine whether these materials (PLA/HH, PLA/ECO, and PLA/HH/ECO) are suitable alternatives in food packaging applications. Oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) measurements can be used in accordance with international standards to evaluate the barrier properties of prepared biocomposites.

5.2.4. Compostability and biodegradability of the prepared biocomposites

Lastly, the biodegradability and compostability of the prepared biocomposites should be explored. This would show the effect of bio-based additives on the degradation process of the polymer. Simulated lab-scale composting conditions can be used to determine the compostability and the degree of disintegration of the PLA-based samples. These tests can be done in mesophilic or thermophilic incubation periods to determine the compostability of the sample by simple gravimetric measurements. Additionally, enzymatic degradation of PLA samples can be explored by using the enzymes that can hydrolyze PLA, as reported in the literature [137].

The future work described above could expand the research on PLA-based biocomposites as a green alternative to non-biodegradable conventional plastics. This transition to biopolymers and biocomposites could lead to a potential reduction in plastic waste. Although there are numerous challenges to be overcome to allow biopolymers such as PLA to be viable alternatives to synthetic polymers on an industrial scale, the work described in this study is a step forward toward creating a sustainable world.

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Appendices

Appendix A: Supplementary information

Figure S1. Received hemp hurds (a), untreated hemp hurd powder (UHH) (b), treated hemp hurd powders including AHH1(c), AHH3 (d), APHH1 (e), and APHH3 (f)

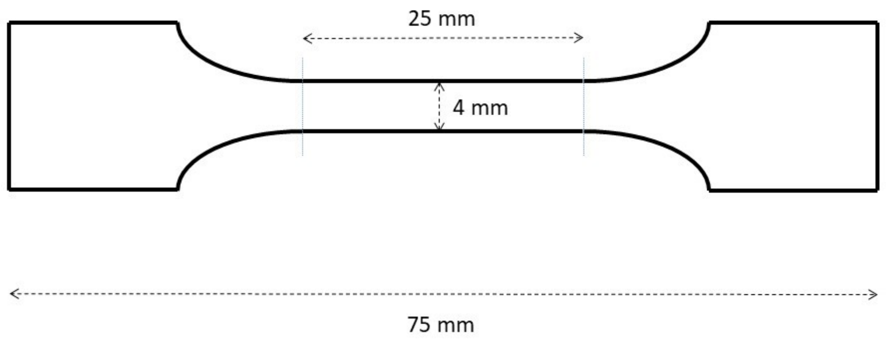

Figure S2. The schematic of dumbbell-shaped specimen for tensile test

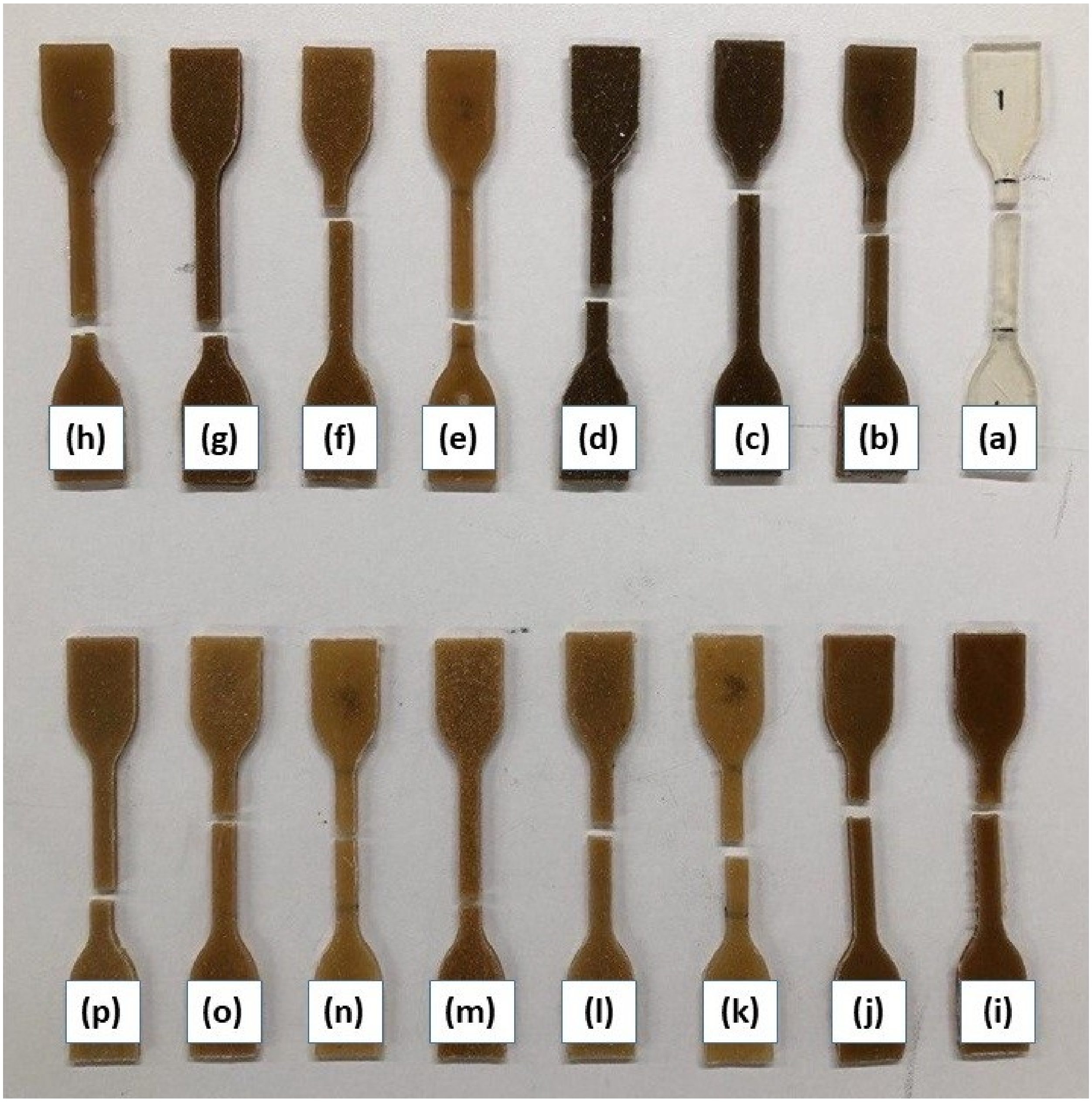

Figure S3. Tensile testing specimens after test; PLA (a), PLA/5UHH (b), PLA/10UHH (c), PLA/15UHH (d), PLA/5AHH1 (e), PLA/10AHH1 (f), PLA/15AHH1 (g), PLA/5AHH3 (h), PLA/10AHH3 (i), PLA/15AHH3 (j), PLA/5APHH1 (k), PLA/10APHH1 (l), PLA/15APHH1 (m), PLA/5APHH3 (n), PLA/10APHH3 (o), and PLA/15APHH3 (p)

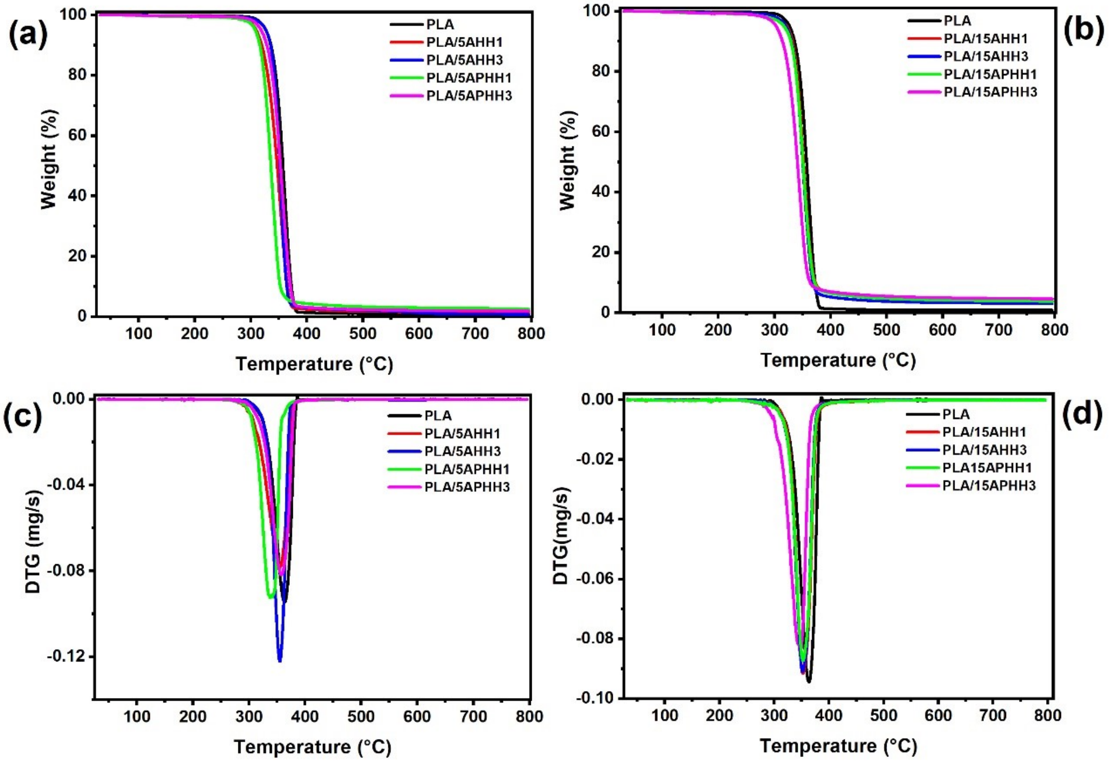

Figure S4. TGA thermograms of PLA and its biocomposites for 5 wt % (a) and 15 wt % (b) filler loading; DTG thermograms corresponding to PLA and its biocomposites for 5 wt % (c) and 15 wt % (d) filler content

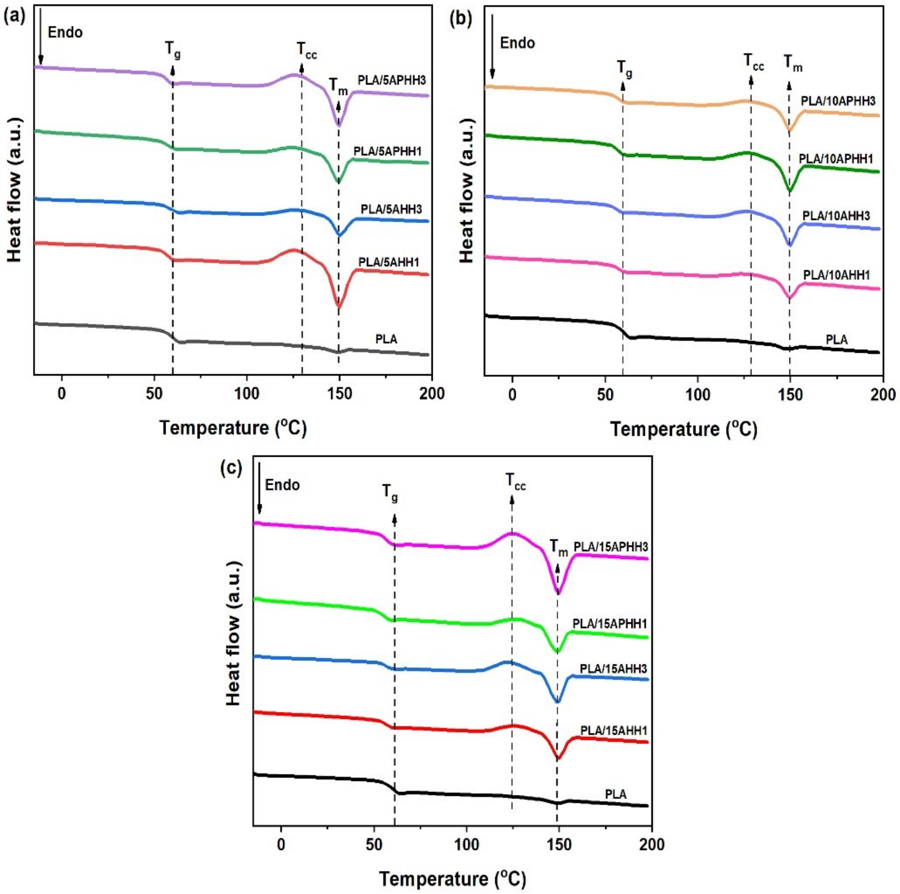

Figure S5. DSC thermograms of PLA and its biocomposites for (a) 5 wt %, (b) 10 wt %, and (c) 15 wt % filler content

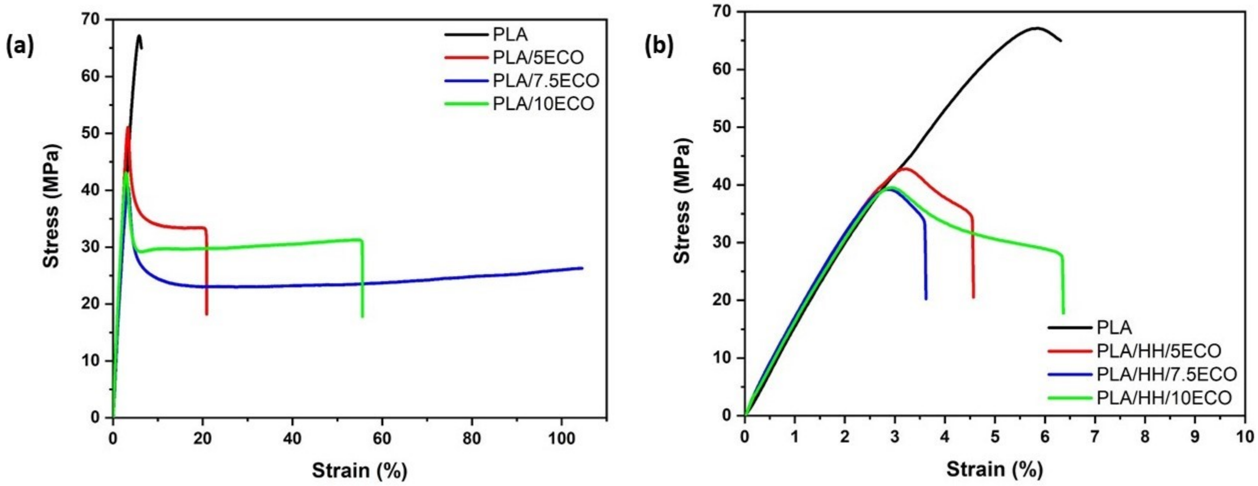

Figure S6. Stress-strain curves of (a) PLA/ECO and (b) PLA/HH/ECO biocomposites

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