Development of Antibacterial Hemp Hurd/Poly(Lactic Acid) Biocomposite for Food Packaging

A thesis submitted by

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Abstract

Contemporary research in food packaging is being progressively focused on the development of biodegradable food packaging from biobased materials for exploring alternatives to traditional, non-biodegradable petroleum based plastics. Consequently, bioplastics are increasingly gaining attention in the food packaging industry because of their potential of biodegradability and versatility in processing. The utilization of bioplastics however is limited because of their inherent shortcomings in thermal and mechanical stability. Recently, bio-derived fillers and plant fibres are being extensively used to address the thermo-mechanical stability and to lower the overall material cost in comparison to the baseline bioplastics. Incorporation of biobased fillers and functional nanoparticles to bioplastics not only offers functionality but also enhances the cost-to-performance ratio of the biocomposites. To that end, this study focused on the development of cost effective, biodegradable, and functional food packaging material.

Poly(lactic acid) has been used in food packaging to replace conventional petroleum based plastics, because it possesses higher mechanical properties, greater versatility in process selection and it is deemed safe for use in food contact. However, apart from the high cost, a major shortcoming of poly(lactic acid) is a slow recrystallization, and hence often requiring an added nucleating agent. The addition of low cost biobased filler to poly(lactic acid) not only lowers the overall material cost but also accelerates crystallization kinetics acting as a nucleating agent.

Industrial hemp hurd is explored as a biobased filler with poly(lactic acid) for biocomposites to lower material cost and to address environmental concerns associated with plastic recycling. However, a major concern for the combination of biobased fillers with polymer matrices to produce biocomposites is the weak fibre-matrix interfacial bonding. In recent years, several forms of glycidyl methacrylate-grafted polyolefins have been prepared through reactive extrusion or solution copolymerization to address this issue. The glycidyl methacrylate grafted copolymer is a potential compatibilizing agent for reducing the interfacial incompatibility in biocomposites. Hence, development of functional biocomposites for food packaging with poly(lactic acid) as bioplastic matrix, hemp hurd as biobased filler and glycidyl methacrylate as compatibilizer was the goal of this study.

Accordingly, a biocomposite was developed using extrusion and injection moulding utilizing hemp hurd and poly(lactic acid) with properties comparable to poly(lactic acid) with grafting-based interfacial compatibilization. Interfacial compatibility between poly(lactic acid) and hemp hurd increased with grafted glycidyl methacrylate in comparison to the non-compatibilized control, as corroborated by scanning electron microscopy fractography. The mechanical properties showed increases in the glycidyl methacrylate-grafted hemp hurd/poly(lactic acid) biocomposite, retaining 94% of the neat polymer strength, with increases in crystallinity at 20% (w/w) loading of hemp hurd. The impact strength data demonstrated that the addition of GMA possesses the potential of improving physical and mechanical properties of HH/PLA composites. The onset of thermal decomposition of the biocomposites obtained through TGA was marginally lower than that of neat PLA.

The antibacterial property of hemp hurd is anecdotally reported, but not systematically investigated and reported. In this study, the antibacterial activity of hemp hurd against *Escherichia coli* was investigated. The antibacterial activity of hemp hurd inhibiting the growth of *E. coli* was significant. To further increase the antibacterial efficacy of hemp hurd, silver nanoparticles was encapsulated into hemp hurd that exhibited high effectiveness. The silver nanoparticles were synthesized into the hemp hurd using a proprietary method developed in collaboration with Ecofibre Pty Ltd.

The inclusion of glycidyl methacrylate further assisted in elastic moduli and strength increase at 10–30 wt. % fraction of silver nanoparticle-loaded hemp hurd in poly(lactic acid), with 20 wt. % hemp hurd-filled biocomposite exhibiting the highest range of properties within the biocomposites investigated. Effective antibacterial activity was achieved with distinct decreases of 85% and 89% in bacterial growth at 0.025 wt. % and 0.05 wt. % loading of silver nanoparticle in the biocomposite. The biocomposites also maintained a safe level of heavy metal migration at 0.20–3.08 mg/kg which meets the European Union (EU) legislation (2002/72/EC), substantially lower than the permitted value of 60 mg/kg. Overall, the properties of these developed biocomposites demonstrated discernible potential in development of food packaging applications.

Cost-benefit analysis was performed to assess the viability in commercial manufacturing for producing rigid food packaging. The biocomposite sensitivity and financial analyses provided data on the degree and magnitude of uncertainties related to investment to afford better product design, and establish the potential of PLA-industrial hemp biocomposites for food packaging applications.

The findings of this study could create a platform upon which packaging designers, food scientists and engineers could initiate to employ biobased materials in their food packaging solutions.

Certification of Thesis

This thesis is entirely the work of Belas Ahmed Khan except where otherwise acknowledged. The work is original and has not previously been submitted for any other award, except where acknowledged.

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Statements of Contributions

The following detail the share of co-authors in the presented publication in this thesis:

- **Khan, B. A**, Warner, P and Wang, H. (2014). Antibacterial Properties of Hemp and Other Natural Fibre Plants: A Review. BioResources Vol. 9, Issue 2, pp 3642-3659

BAK was responsible for 85% literature review, 85% analysis and interpretation of data, and 100% drafting and revising the final submission; PW was responsible for 5% literature review, 5% analysis and interpretation of data and 20% of editing the manuscript and providing important technical inputs; HW was responsible for 10% literature review, 10% analysis and interpretation of data, and 80% of editing the manuscript and providing important technical inputs. In this article, overall contributions by BAK, PW and HW are 85%, 5% and 10% respectively.

- **Khan, B. A**., Chevali, V. S., and Wang, H. (2016). Review on Potential Food Packaging Applications of Biodegradable Biocomposites. *Intended to submit in Composites Part B*

BAK was responsible for 75% literature review, 75% analysis and interpretation of data, and 100% drafting and revising the final submission; VSC was responsible for 15% literature review, 15% analysis and interpretation of data, and 80% of editing the manuscript and providing important technical inputs; HW was responsible for 10% literature review, 10% analysis and interpretation of data, and 20% of editing the manuscript and providing important technical inputs. In this article, overall contributions by BAK, VSC and HW are 75%, 15% and 10% respectively.

- **Khan, B. A**, Wang, J., Warner, P and Wang, H. (2015). Antibacterial Properties of Hemp Hurd Powder against *E. coli*. Journal of Applied Polymer Science, Vol. 132, Issue 10

BAK was responsible for 75% designing the experimental set-up, 70% experimental works, analysis and interpretation of data, and 100% drafting and revising the final submission; JW was responsible for 10% designing the experimental set-up, 10% experimental works, analysis and interpretation of data, and 50% of editing the manuscript and providing important technical inputs; PW was responsible for 5% designing the experimental set-up, 10% experimental works, analysis and interpretation of data, and 10% of editing the manuscript and providing important technical inputs; HW was responsible for 10% designing the experimental set-up, 10% experimental works, analysis and interpretation of data, and 40% of editing the manuscript and providing important technical inputs. In this article, overall contributions by BAK, JW, PW and HW are 75%, 10%, 5% and 10% respectively.

- **Khan, B. A**, Na, H., Chevali, V. S., Zhu, J., Warner, P and Wang, H. (2016). Glycidyl Methacrylate-Compatibilized Poly(lactic acid)/Hemp Hurd Biocomposites: Processing, Crystallization, and Thermo-mechanical Response. *Chinese Journal of Polymer Science, In Submission*

BAK was responsible for 60% designing the experimental set-up, 60% experimental works, analysis and interpretation of data, and 100% drafting and revising the final submission; HN was responsible for 10% designing the experimental set-up, 10% experimental works, analysis and interpretation of data, and 30% of editing the manuscript and providing important technical inputs; VSC was responsible for 10% designing the experimental set-up, 10% experimental works, analysis and interpretation of data, and 30% of editing the manuscript and providing important technical inputs; JZ was responsible for 5% designing the experimental set-up, 5% experimental works, analysis and interpretation of data, and 10% of editing the manuscript and providing important technical inputs; PW was responsible for 5% designing the experimental set-up, 5% experimental works, analysis and interpretation of data, and 10% of editing the manuscript and providing important technical inputs; HW was responsible for 10% designing the experimental set-up, 10% experimental works, analysis and interpretation of data, and 20% of editing the manuscript and providing important technical inputs. In this article, overall contributions by BAK, HN, VSC, JZ, PW and HW are 60%, 10%, 10%, 5%, 5% and 10% respectively.

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BAK was responsible for 60% designing the experimental set-up, 60% experimental works, analysis and interpretation of data, and 100% drafting and revising the final submission; VSC was responsible for 10% designing the experimental set-up, 15% experimental works, analysis and interpretation of data, and 50% of editing the manuscript and providing important technical inputs; HN was responsible for 10% designing the experimental set-up, 5% experimental works, analysis and interpretation of data, and 10% of editing the manuscript and providing important technical inputs; JZ was responsible for 5% designing the experimental set-up, 5% experimental works, analysis and interpretation of data, and 10% of editing the manuscript and providing important technical inputs; PW was responsible for 5% designing the experimental set-up, 5% experimental works, analysis and interpretation of data, and 10% of editing the manuscript and providing important technical inputs; HW was responsible for 10% designing the experimental set-up, 10% experimental works, analysis and interpretation of data, and 20% of editing the manuscript and providing important technical inputs. In this article, overall contributions by BAK, VSC, HN, JZ, PW and HW are 60%, 15%, 5%, 5%, 5% and 10% respectively.

- **Khan, B. A**, Alam, K., Chevali, V. S., and Wang, H. (2016). Assessing technical and financial viability of a new generation antibacterial biocomposite: The case of food packaging industry. *Journal of Cleaner Production, Submitted*

BAK was responsible for 70% designing the experimental set-up, 70% experimental works, analysis and interpretation of data, and 100% drafting and revising the final submission; KA was responsible for 15% designing the experimental set-up, 15% experimental works, analysis and interpretation of data, and 40% of editing the manuscript and providing important technical inputs; VSC was responsible for 10% designing the experimental set-up, 10% experimental works, analysis and interpretation of data 40% of editing the manuscript and providing important technical inputs; HW was responsible for 5% designing the experimental set-up, 5% experimental works, analysis and interpretation of data, and 20% of editing the manuscript and providing important technical inputs. In this article, overall contributions by BAK, KA, VSC and HW are 70%, 15%, 10% and 5% respectively.

Statement of Contributions signed by each co-author of published papers are enclosed in the Appendix A.

Table of Contents

List of Abbreviations

Acrylonitrile butadiene styrene (ABS)
Benefit cost ratio (BCR)
Colony forming units (CFU)
Cost-benefit analysis (CBA)
Differential scanning calorimetry (DSC)
Escherichia Coli (*E. coli*)
Ethylene vinyl acetate (EVA)
Ethylene vinyl alcohol (EVOH)
Expanded polystyrene or EPS
Fluoropolymers (PCTFE/PTFE)
Fourier-transform infrared spectroscopy (FTIR)
Gas chromatography (GC)
Gas chromatography–mass spectroscopy (GC-MS)
Glycidyl methacrylate (GMA)
Greenhouse gas (GHG)
Hemp Hurd (HH)
High density polyethylene (HDPE)
High nitrile polymers (HNP)
Hydroxyl-butyrate (HB)
Hydroxyl-valerate (HV)
Inductively coupled plasma optical emission spectrometry (ICP-OES)
Inductively coupled plasma-mass spectrometry (ICP-MS)
Life cycle assessment (LCA)
Liquid chromatography (LC)
Liquid chromatography-mass spectroscopy (LC-MS)
Low density polyethylene (LDPE)
Modified atmosphere packaging (MAP)
Net present value (NPV)
Poly(butylene adipate-co-terephthalate) (PBAT)
Poly(butylene succinate) (PBS)
Poly(butylene succinate-co-adipate) (PBSA)
Poly(caprolactone) (PCL)
Poly(epichlorohydrin-co-ethylene oxide) (PEEO)
Poly(esteramide) (PEA)
Poly(hydroxyl alkanoate) (PHA)
Polyamides (PA)
Polyethylene (PE)
Polyethylene terephthalate (PET or PETE)
Polylactide (PLA)
Polymethyl pentene (TPX)
Polypropylene (PP)
Polystyrene (PS)
Polyurethane (PU)
Polyvinyl acetate (PVA)
Polyvinyl chloride (PVC)
Polyvinylidene chloride (PVDC)
Scanning electron microscopy (SEM)
Silver Nanoparticles (AgNPs)
Styrene butadiene (SB)
Tetrahydrocannabinol (THC)
Thermogravimetric analysis (TGA)
Thermoplastic starch (TPS)
X-ray diffraction (XRD)

1. INTRODUCTION

Plastics are advantageous in providing effective barrier properties in food packages of low density (low weight) and high durability at low cost (Birley, 1982) holding the highest market share of 37% by value (Muncke, 2012). Typical plastics used in food-packaging are thermoplastic polymers, including polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET or PETE), ionomers, ethylene vinyl acetate (EVA), polyamides (PA), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), polystyrene (PS), styrene butadiene (SB), acrylonitrile butadiene styrene (ABS), ethylene vinyl alcohol (EVOH), polymethyl pentene (TPX), high nitrile polymers (HNP), fluoropolymers (PCTFE/PTFE), cellulose-based materials, polyvinyl acetate (PVA) (Coles et al., 2003). In the European packaging market, PE constitutes the highest proportion of consumption, with about 54% of the market by weight, and four others, PP, PET, PS (including expanded polystyrene or EPS) and PVC, comprise most of the remaining 46% (Coles et al., 2003).

However, recycling of plastic food packaging materials is often impracticable as they are contaminated by foodstuff and biological substances after use and cannot be reclaimed in an economically viable (Valentina S., 2008) manner, often leading to landfilling (Kirwan, 2003). This growing environmental concern has driven packaging materials to be produced to be eco-friendly. Consequently, biodegradability, hence, is now a functional requirement and an important environmental attribute. Biodegradable polymers, derived from renewable sources are used, breaking down at disposal to produce carbon dioxide, water, and compost (Tharanathan, 2003).

Among the biodegradable/compostable polymers, polylactide (PLA) is recognized as a key polymer (Auras et al., 2006) for industrial plastic applications because of its processability ease (Lee et al., 2009). PLA is a strong candidate to replace conventional petroleum-based polymers and often possesses higher mechanical properties and greater versatility in process selection (Lee et al., 2009, Yu et al., 2014, Graupner et al., 2009, Frone et al., 2013). Apart from the high cost, the major shortcomings of PLA in its unfilled form are the moderate to low mechanical and thermal stabilities (Huda et al., 2005) for biocomposite applications. Heat resistant PLA plastic products often require injection moulding with rapid recrystallization, and hence require an added nucleating agent (Drumright et al., 2000). In recent years, considerable research effort has been devoted to the development of new eco-friendly, sustainable bioproducts using PLA, including biocomposite applications for automotive, building, and appliance industries. PLA has been used in food packaging research and development (Gupta and Kumar, 2007), because it is deemed safe for use in food contact (Conn et al., 1995).

Synthetic and bio-based fillers are often added to polymers to lower cost at acceptable physical and mechanical properties. However, the supply of natural resources is depleting, and demand for renewable raw materials is increasing, therefore, responsible use of available natural fibres and fillers is critical for sustainable development. Plant co-products that avoid the use of new agricultural lands, preclude competition with food sources, and provide value addition to farmers (Beaugrand et al., 2014) are highly desirable. For instance, industrial hemp fibres exhibit potential as a composite reinforcement (Ku et al., 2011) because of their high specific mechanical properties, however, the usage of industrial hemp hurd as a biocomposite filler is evolving (Karus and Vogt, 2004). In the hemp fiber production, decortication of the hemp stems provides two biomass products, i.e., the hemp fiber and hemp hurd (HH). HH is the woody core of the stem (approximately 70% of the stem mass), which is used in applications such as animal bedding or as hempcrete for construction. The application of HH as a filler for biocomposites not only adds value to the material, but also addresses environmental concerns (Wang et al., 2011). HH bears substantial potential as a biobased filler for compounding with PLA as biocomposites for use in food packaging applications.

The main concern of biocomposites is the incompatibility between hydrophilic natural fibers and hydrophobic thermoplastics, which results in the weak adhesion at the two-phase interface and leads to inadequate mechanical and physical properties (Xie et al., 2010). Thus, the critical issue concerning hemp hurd as structural fillers to promote the overall properties of PLA composites as well as material cost reduction is essentially related to the improvement of interfacial compatibility between these components. Typically, surface modification of cellulose (Faruk et al., 2012) or addition of compatibilizers such as isocyanates (Chen et al., 2008, Xu et al., 2012, Nyambo et al., 2011) and maleated PLA (Wang et al., 2014) are the common practices to enhance the interfacial compatibility between PLA and lignocellulosic fillers.

Glycidyl methacrylate (GMA) is a well-known bifunctional monomer, which consists of acrylic and epoxy groups. The epoxy group of GMA can react with hydroxyl and carboxyl groups, whereas acrylic groups show the capability of free-radical grafting of GMA onto the polymer chain (Xu et al., 2012). In recent years, several forms of GMA-grafted polyolefins have been prepared through reactive extrusion or solution copolymerization (Burton et al., 2010, Xu et al., 2012). The GMA-grafted copolymer is a potential compatibilizing agent for reducing the interfacial incompatibility in polymer blends or as a coupling agent in biocomposites.

To provide shelf-life extension to packaged food, innovative active and intelligent packaging concepts are being developed, including incorporating oxygen, moisture, and ethylene scavengers for oxygen, moisture, and ethylene sensitive foods, respectively, use of carbon dioxide or ethylene emitters in other foods, flavour imparting or scavenging chemicals, and antimicrobial agents for microbiological safety of food (Cha and Chinnan, 2004). The application of antimicrobial agents to packaging can delay or even prevent the growth of microorganisms on the product surface and, hence, lead to an extension of the shelf life. Antibacterial packaging is a form of active packaging that interacts with the product or the headspace between the package and the food system, achieve extended shelf life (Appendini and Hotchkiss, 2002). To that end, antibacterial packaging can play an important role in reducing the risk of pathogenic bacterial contamination as well as in extending the shelf life of minimally processed foods.

Anecdotal evidence has shown that HH does possess antibacterial properties, however, this aspect has never been systematically investigated. As the potential of HH for antibacterial packaging has not been explored yet, further research and development is important. In addition, it is well known that nanoparticles of silver, copper and zinc exhibit antibacterial function (Ren et al., 2009). Among these, silver nanoparticle is known to possess the highest antibacterial capacity, with long-term biocide properties, low volatility and low toxicity to eukaryotic cells (Fernández et al., 2010), hence, often incorporated into food packaging. Heavy metal migration limits from packaging materials into food is controlled by strict regulations such as European Union Directive 2002/72/EC (Commission, 2006, Byrne, 2002) to address associated health hazards. The ultimate goal of scientific studies today is to reduce the heavy meatal migration into food and thereby to minimize the hazards to consumer health, yet preserving an effective antibacterial efficacy (Llorens et al., 2012).

The main goal of this study was to develop antibacterial biocomposites utilizing extrusion and injection moulding for food packaging with PLA as bioplastic matrix and HH as biobased filler, to reduce material cost as well as a carrier vehicle for an antibacterial agent. Therefore, multifunctional HH was critically characterized, including investigation of antibacterial efficacy. To further increase the antibacterial efficacy of HH, silver nanoparticles were synthesized and loaded into HH, and incorporated to PLA, producing antibacterial biocomposite. This study also entailed functionalizing the fibre/matrix interface for increased adhesion between the hydrophobic PLA and hydrophilic HH using GMA. The analysis and characterization of mechanical, chemical and thermal properties, and antibacterial efficacy of the biocomposites were investigated. An assessment of technical and financial viability of the biocomposite for food packaging application was conducted to determine commercial viability of the developed biocomposite for packaging.

1.1. Research Questions

The main research questions that were addressed through the course of this study are:

- To what extent hemp hurd is antibacterial? Why?
- How incompatibility of PLA and HH affect the properties of their composites?
- How GMA contributes to improve compatibility of HH and PLA in the biocomposites?
- How silver nanoparticles loading contributes to the antibacterial property of biocomposite?
- Is the antibacterial silver nanoparticle-loaded HH/PLA biocomposites technically and financially viable for food packaging application?

1.2. Research Objectives

The overall aim of this study was to develop an antibacterial HH/PLA biocomposites for food packaging. This research was carried out to meet the following objectives:

- To critically analyse HH including investigation of its antibacterial property
- To determine the optimum ratio of PLA and HH in the biocomposite through parametric study by analysing the effects that stem from processing trials to obtain the desired set of physical and mechanical properties
- To investigate the processing, crystallization, and thermo-mechanical response of compatibilized HH/PLA biocomposites
- To synthesize silver nanoparticles to be encapsulated into HH, and compound with PLA to produce an antibacterial biocomposite
- To investigate the processing and properties of antibacterial silver nanoparticle-loaded HH/PLA biocomposites

- To assess the technical and financial viability of the biocomposites for food packaging application

1.3. Thesis Organisation

This thesis is comprised of six chapters. The thesis chapters are presented in a logical and coherent sequence leading to an argument that supports the main findings of the thesis, described as follows:

Chapter 1: Introduction

This chapter introduces the research theme and motivations to pursue this study including objectives and organisation of this thesis using key background studies from literature.

Chapter 2: Literature Review

This chapter focuses on survey of literature constituting the development of cost effective, eco-friendly, antibacterial biocomposite material design for food packaging applications requiring insightful understanding into the critical issues associated with food packaging materials. This chapter comprises of two review articles as literature review. The first article focuses on potential application of biodegradable biocomposites as primary food packaging material. The second article is an extensive literature review on antibacterial properties of hemp and other natural fibre plants. The articles included in this chapter are as follows:

- Khan, B. A., Chevali, V. S., and Wang, H. A Review of Bioplastic Composites for Food Packaging. *In Submission*

- Khan, B. A, Warner, P and Wang, H. (2014). Antibacterial Properties of Hemp and Other Natural Fibre Plants: A Review. BioResources Vol. 9, Issue 2, pp 3642-3659

Both this articles provide a comprehensive understanding of the current research status including challenges regarding biobased food packaging and use of hemp hurd as functional biobased filler. The articles provides clear association to the conceptual theory and methodologies adopted in this study.

Chapter 3: Conceptual Framework and Methodology

This chapter describes the conceptual framework and methodology used for analysis and characterization of biocomposites. This chapter provides the methodology of material selection, processing and characterization techniques chosen to pursue the research goal.

Chapter 4: Material Development and Properties Analysis

This chapter contains four studies addressing the objectives of this research and presented as research articles. Each article within this chapter are linked to the conceptual theory and methodologies adopted in this study contributing to the advancement of the research area.

The first article is the characterization of HH that covers investigations on the chemical, thermal, morphology and antibacterial properties of the HH.

- Khan, B. A, Wang, J., Warner, P and Wang, H. (2015). Antibacterial Properties of Hemp Hurd Powder against *E. coli*. Journal of Applied Polymer Science, Vol. 132, Issue 10

The second paper covers the physical and thermal properties of the HH/PLA biocomposites focusing on interfacial bonding.

- Khan, B. A, Na, H., Chevali, V. S., Zhu, J., Warner, P and Wang, H. Glycidyl Methacrylate-Compatibilized Poly(lactic acid)/Hemp Hurd Biocomposites: Processing, Crystallization, and Thermo-mechanical Response. *In Submission*

The third article provides research outcome on fabrication and characterization of antibacterial silver nanoparticles loaded HH/PLA biocomposites.

- Khan, B. A, Chevali, V. S., Na, H., Zhu, J., Warner, P and Wang, H. (2015). Processing and Properties of Antibacterial Silver Nanoparticle-loaded Hemp Hurd/Poly(lactic Acid) Biocomposites. Composites Part B: Engineering, Vol. 100, pp 10-18

The fourth article deals with the assessment of technical and financial viability of the biocomposite for food packaging.

- Khan, B. A, Alam, K., Chevali, V. S., and Wang, H. Assessing Technical and Financial Viability of a New Generation Antibacterial Biocomposite: The case of food packaging industry. *In Submission*

Chapter 5: Conclusions and Future Works

This chapter summarises the findings and contribution of this study and proposes recommendations for future works that will constitute an extension of the current thesis.

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2. PUBLICATIONS FORMING LITERATURE REVIEW

2.1 Paper-I: A Review of Bioplastic Composites for Food Packaging

Khan, B. A., Chevali, V. S., and Wang, H. (2016). A Review of Bioplastic Composites for Food Packaging. *In Submission*

The overall objective of this review article was to provide a comprehensive and critical review of the literature in the area of biocomposites with a bioplastic matrix for potential food packaging application. This article provides analysis on the existing packaging plastics including their properties and unique characteristics which made them appropriate for specific food packaging application, bioplastics including their current food packaging applications, potential biobased fillers, development of biocomposites with bioplastics and biobased fillers including related concerns, contemporary challenges associated with current food packaging such as material-food interaction and environmental impact. The design and manufacturing issues of biocomposites for food packaging in view of preferred properties and attributes are also discussed.

A Review of Bioplastic Composites for Food Packaging

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Abstract

Bioplastics are increasingly gaining attention in the food packaging industry because of their potential of biodegradability and versatility in processing. The utilization of bioplastics however is limited because of their inherent shortcomings in thermal and mechanical stability. Recently, bio-derived fillers and plant fibers are being extensively used to address the thermo-mechanical stability and to lower the overall material cost in comparison to the bioplastics. The aim of the current review is to provide a comprehensive and critical review of the literature in the area of biocomposites with a bioplastic matrix. This review will address the bottom-up development of bioplastic biocomposites from the perspective of materials engineering, focusing on the materials selection, contemporary challenges for food packaging plastics, and critically discuss the design and manufacturing strategies for these biocomposites. Advances in food packaging plastic property development will be presented along with the future directions and conclusions.

Keywords

Biopolymers, Natural Fibers, Packaging, Processing, Mechanical Design

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1 Introduction

Over the past few decades, the use of plastics as food packaging materials has increased tremendously because of their advantages over other traditional packaging materials [1, 2]. 42% of the global plastics market is constituted by packaging, with sales volume increasing from 5 million tons in the 1950s to nearly 100 million tons today. Packaging industry is worth about 2% of Gross National Product in some developed countries [3]. Packaging is the largest demand segment of plastic market since plastic packaging provides many advantages including strength and stiffness, barrier to oxygen and moisture, resistance to food component attack and flexibility.

Food packaging can be classified into three categories, i.e., primary, secondary and tertiary packaging, where primary packaging materials have direct contact with foods, secondary packaging used for physical protection of the product, and tertiary packaging incorporates the secondary packages in a final transportation package system [4]. Henceforth, the word packaging will be meant as primary packaging in this paper.

Food packaging is designed with the purpose of containing food in a cost-effective manner which will abide to the industry standards and will cater to the customer requirements while maintaining food safety and alleviating environmental impact [5]. The right selection of packaging materials and technologies is very important to preserve product quality and freshness during distribution and storage. Plastics, paper, glass and metals are traditionally used packaging materials (*Figure 1*) where plastic packaging (rigid & flexible) holds the highest market share (by market value).

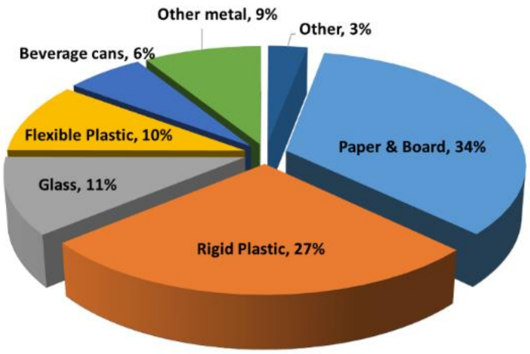

Figure 1. Market share of food packaging materials (by market value) (Source: Rexam consumer packaging report 2011/12) [6]

In the last decade, development and application of bioplastics for food packaging has attained enormous interest. Recently, the packaging industry is invested in using bioplastics from bio-derived materials from their traditional focus on creating compostable/biodegradable materials [7]. Thus, bio-based bioplastics and their biocomposites (filled with natural fibers/fillers) are strong potential candidates for future food packaging.

2 Bioplastics and Biocomposites in Packaging

According to the European Bioplastics Organization, bioplastics can be defined as plastics based on renewable resources (bio-based) or as plastics which are biodegradable and/or compostable. *Figure 2* presents the classifications of bioplastics. Bioplastics can be broadly classified into three main groups depending on the source and biodegradability: (i) bio-based and non-biodegradable, (ii) bio-based and biodegradable/compostable, and (iii) fossil-based and biodegradable/compostable.

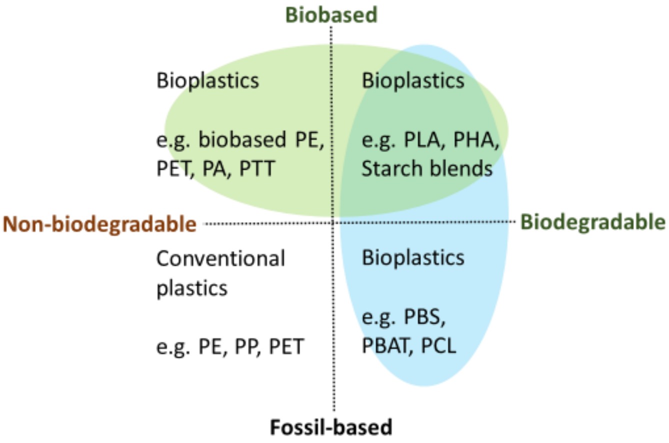

Figure 2. Types of bioplastics (Source: European Bioplastics)

The global bioplastics production capacity is expected to exceed over 6.5 million tons by 2018 (source: European bioplastics). *Figure 3* presents worldwide bioplastics production capacities (in 2013) according to polymer type which indicates that starch and its blends, poly(lactic acid) (PLA) and various types of polyhydroxyalkanoates (PHAs) are of the highest importance among bio-based and biodegradable polymers. The production of conventional polymers such as PE or PET based on renewable resources also gains gradual importance. These are not biodegradable; however, their performance is the same as that of their fossil-based counterparts.

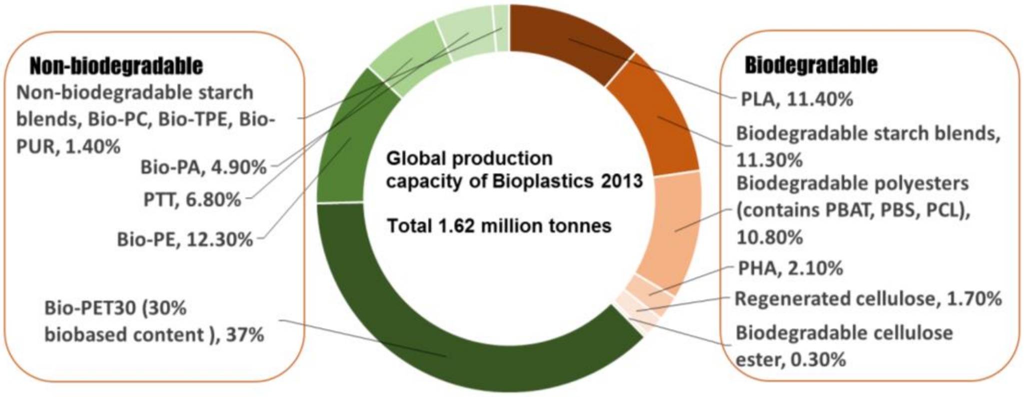

Figure 3. Global production capacity of bioplastics in 2013 (Source: European Bioplastics)

Currently, scientists and engineers successfully are engaged with research and development of technologies that will decrease costs and optimize the performance of bio-based products. Environmental concerns are strengthening the attention in agricultural and forestry resources as alternative feedstocks [4]. Food packaging is a key market segment for bioplastics, where their use will be a natural choice once they became available as viable commercial products.

2.1 Conventional Plastic Packaging

In the United States, the plastics industry is the third largest manufacturing industry at 10.9 billion US dollars [8]. Although this area includes many industrial plastics, the food packaging industry comprises almost a 20% of the net revenue of the plastic industry where polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) are the key constituents of common food packaging plastics [9]. *Table 1* shows properties of some typical thermoplastic polymers used in plastic food packaging.

Table 1. Properties of typical thermoplastic polymers used food packaging [10, 11]

Properties	PP	LDPE	HDPE	PS
Density	0.90–0.92	0.91–0.93	0.94–0.96	1.04–1.06

Water absorption (% mass gain) (24 h @ 20°C)	0.01–0.02	<0.02	0.01–0.20	0.03–0.10
T_g (°C)	−10 to −23	−125	−133 to −100	--
T_m (°C)	160–176	105–116	120–140	110–135
Heat deflection temperature (°C)	50–63	32–50	43–60	< 220
Coefficient of thermal expansion (mm/mm/°C × 10^5)	6.8–13.5	10	12–13	6–8
Tensile strength (MPa)	26.0–41.4	40–78	14.5–38	25–69
Elastic modulus (GPa)	0.95–1.77	0.055–0.38	0.4–1.5	4–5
Elongation (%)	15–700	90–800	2.0–130	1–2.5
Izod impact strength (J/m)	21.4–267	>854	26.7–1068	1.1

Plastics are effective in providing barrier properties in packaging of low density (low weight) and high durability at low cost [12]. The types of plastics used in food-packaging are PE, PP, PET, PVC, PS, ionomers, ethylene vinyl acetate, polyamides, polyvinylidene chloride, styrene butadiene, acrylonitrile butadiene styrene, ethylene vinyl alcohol, polymethyl pentene, high nitrile polymers, fluoropolymers, and polyvinyl acetate [13]. In the European packaging market, PE makes the highest proportion of consumption, with about 56% of the market by volume, and four others, i.e., PP, PET, PS (including expanded polystyrene or EPS) and PVC, comprise the remaining 46% [13].

The utilization and market share of a specific plastic is a function of unique property characteristics. PET exhibits exceptional tensile and yield strength properties as well as being transparent after processing, ideal for cold beverages since the melting temperature is low [14]. HDPE is used for clouded containers or bottles for milk where mechanical strength is also needed, however, clarity is not required [15]. The use of PVC is common for clear plastic wrapping because of its stretchability as well as the ease of formability as sheets [16]. LDPE is used for food storage bags owing to its stretch capacity as well as barrier properties [17]. PP is used in rigid containers such as baby bottles and cups, and bowls because of its high strength properties [18]. PS is commonly used in Styrofoam food containers and cups as well as meat and egg trays that require a rigid form and heat resistance [19].

Plastic packaging materials are also often contaminated by foodstuff and biological substances, which increases the cost of recycling, causing it to be unviable [20], driving landfilling of thousands of tons of used plastic packaging materials every year [21]. The opposition to landfilling has spurred increased environmental awareness leading to the development of novel eco-friendly packaging materials that are biodegradable and compostable, which are now functional requirements rather than being mere environmental attributes. The obvious choice of plastics for packaging is hence biopolymers that are derived from bio-based renewable plant and animal resources, and from industrial waste streams.

2.2 Biopolymers

Biopolymers are derived from renewable agricultural feedstocks, animal sources, marine food processing industry wastes, or microbial sources. Furthermore, biodegradable biopolymers break down at disposal to produce carbon dioxide, water, and compost [22]. Hence, biopolymer-based packaging is defined as packaging that contains raw materials originating from agricultural and marine sources. There are three such categories of biopolymers: (a) extracted directly from natural raw materials, such as starch, cellulose, protein, and marine prokaryotes; (b) produced by chemical synthesis from bio-derived monomers; (c) produced by microorganisms such as poly(hydroxyl butyrate) and poly(hydroxy valerate) [23]. The various naturally occurring biopolymers of use in composite sheet forming and coating formulations are shown in *Figure 4*. Biodegradable polymers whose monomers and polymers are both obtained by chemical synthesis from fossil resources, e.g., poly(caprolactone) (PCL), poly(esteramide) (PEA), aliphatic co-polyesters such as poly(butylene succinate-co-adipate) (PBSA), and aromatic co-polyesters such as poly(butylene adipate-co-terephthalate) (PBAT).

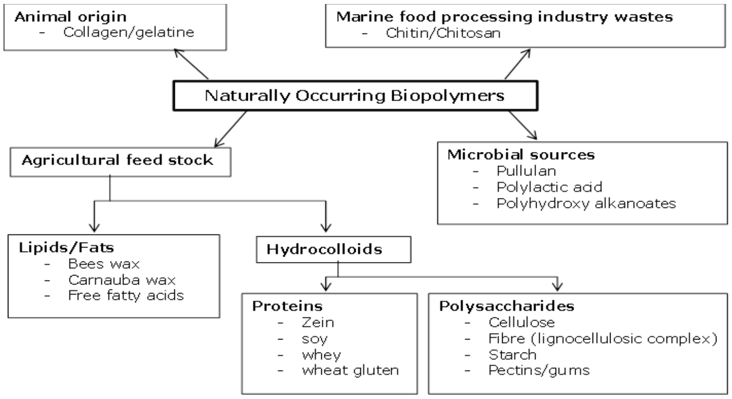

Figure 4. Naturally occurring biopolymers of use in biodegradable packaging films and composites [22].

The field of application of biodegradable polymer in food-contact articles includes disposable cutlery, drinking cups, salad cups, plates, overwrap and lamination film, straws, stirrers, lids and cups, plates and containers for food dispensed at delicatessen and fast-food establishments [20]. *Table 2* shows properties of some biodegradable polymer used in biocomposites.

Table 2. Properties of Biodegradable Polymers used in Biocomposites [11, 24-29]

Property	PEA	PLA	SPI	PHB	PHBV
Density (g/cm^3)	1.18	0.9–1.27	1.2–1.5	1.25	1.25
Elastic modulus (GPa)	0.42	1.5–2.7	0.1	0.93	2.38
Tensile strength (MPa)	16.4	60	6	21	25.9
Elongation (%)	85–119	8	170–236	5.2–8.4	1.4
Melting temperature (°C)	175	160–190	4–8	161	153
Glass transition temperature (°C)	–	56–65		−10	−1

Polyesteramide (PEA), polyhydroxybutyrate (PHB), polyhydroxybutyrate-co-hydroxyvalerate (PHBV), polylactide (PLA) and soy protein isolate resin (SPI)

Among the biodegradable/compostable polymers, polylactide (PLA) is recognized as a key polymer [30] for industrial plastic applications because of its processing ease [31]. Novel eco-friendly, sustainable bio-products using PLA and its biocomposites are fast emerging for automotive, building, and appliance industries, and more importantly as a potential material for food packaging [32], where PLA is deemed to be safe for use in contact with foodstuff [33].

PLA is completely biodegradable when it is composted at 60 ºC and above [34, 35] in a certain condition. The first step of the degradation proceeds through hydrolysis into water-soluble compounds and lactic acid. Subsequently, microorganisms metabolize these products into carbon dioxide, water, and biomass (*Figure 5*) [36]. The biodegradation mechanisms of PLA are an effect of several structure and hydrolysis media aspects. The diffusion coefficient of the soluble oligomers is critical, and dependent on the molar mass, matrix swelling, macromolecular structure, chemical structure, mobility of chains, stereochemistry, molecular weight distribution, and crystallinity. The amorphous domain is vulnerable to the biodegradation attack [37].

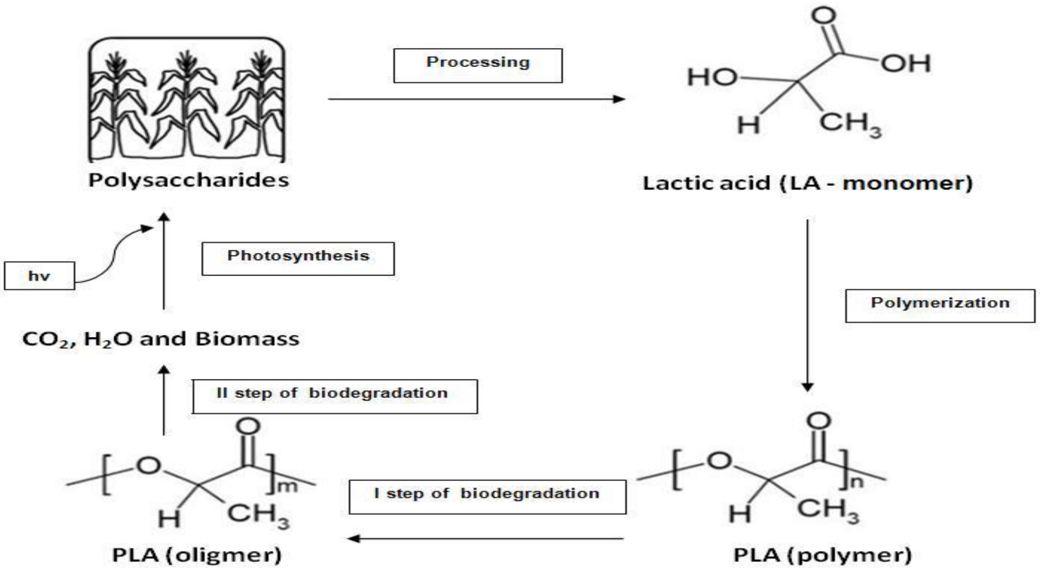

Figure 5. The steps in the life cycle of poly(lactic acid) through degradation [34].

Starch is another extensively available biodegradable natural resource that necessitates high-water content or plasticizers (glycerol, sorbitol) to transform into a plastic-like film material. The plasticized material obtained through the application of thermal and mechanical energy is termed as thermoplastic starch (TPS), which is an alternative for polystyrene (PS). Starch-based thermoplastics such as blends of TPS and synthetic/biodegradable polymer components, such as polycaprolactone, polyethylene-vinyl alcohol, or polyvinyl alcohol are applied in industrial-level processes such as foaming, film blowing, injection molding, blow molding, and extrusion [38-40].

Poly(hydroxyl alkanoates) or PHAs are the polymers of hydroxyalkanoates, gathered as a source of carbon or energy in microorganisms in a state of restrained nutrition. Over 300 microorganisms are known to synthesize and accumulate PHAs [41]. The best known biopolymers are the polyhydroxyalkanoates, commonly polyhydroxy-butyrates, and copolymers of hydroxyl-butyrate (HB), and hydroxyl-valerate (HV) [42].

In addition to PLAs, PHAs, and starch, biopolymers such as zein and gluten (protein) as well as chitosan or forms of cellulose or cellulose derivatives have been explored for their potential in many packaging-related products. Water sensitivity is a clear disadvantage for these biopolymers, however, their proven oxygen barrier characteristics often overshadow this concern [43]. *Table 3* lists the current food packaging applications of neat bioplastics.

Table 3. Current Applications of Bioplastics as Food Packaging [7]

Packaging application	Biopolymer	Ref
PLA[†] Coffee And Tea, Beverages, Carbonated Water, Fresh Juices, Dairy Drinks, Fresh Salads, Freshly Cut Fruits, Whole Fruits, Vegetables, Bakery Goods, Organic Pretzels, Potato Chips, Yoghurt, Frozen Fries, Pasta, Herbs, Prepared Sandwiches, Bread, Organic Poultry	Cardboard Cups Coated With PLA, PLA Cups, PLA Bowls, PLA Bottles, Rigid PLA Trays And Packs, PLA Bags, PLA Jars, PLA Films (Bio-Flex), PLA Packaging, Packaging Paper Bags With PLA Window	[7, 44-50]
Starch-Based[‡] Milk Chocolates, Organic Tomatoes	Cornstarch Trays, Corn-Based Packaging	[50]
Cellulose Kiwi, Potato Chips, Organic Pasta, Sweets	Bio-based Trays Wrapped With Cellulose Film, Metalized Cellulose Film, Cellulose-Based Packaging	[51]

2.3 Blends of Biopolymers

Biopolymer blends today are the focus in biopolymer research [44]. The goal of blending multiple biopolymers is enhancement or modification of a certain application and realizing novel functionalities. However, the fundamental motivation for biopolymer blending is the overarching cost saving, improvements in mechanical properties and impact resistance, and increasing the resistance to aqueous media [45].

[†] http://www.natureworksllc.com

[‡] http://en.european-bioplastics.org

Often, the most pronounced property characteristics are either preserved or enhanced. For example, PHAs are versatile, however expensive, hence their modification involves blending with starch and aims towards the reduction of material costs. The same methodology is valid for PLA as well, where the toughness is improved through the inclusion of elastomers. Conversely, the price of starch is low; however, its mechanical properties are mediocre, and is water sensitive, thus the addressment of these characteristics is important. The underlying philosophy in all of the aforementioned cases is the effective blends exhibiting comparable performances as the baseline material and showing reduced cost or realizing a value addition. Studies have been carried out on different biopolymer blends and types. The area of biopolymer interactions has been the focus of intensive fundamental and applied research in recent time [46]. Such biopolymer combinations may possess unique properties that are different from those of individual components. In the field of biopolymer blends, the two most critical issues in developing biopolymer blend are (1) miscibility or compatibility of the biopolymer blend components, and (2) complete biodegradability of the components.

Published literature addressing biopolymer blends is vast, because of the volume and diversity of these polymers, and additionally because of the increased attention in this research area. The reader is directed to published works on biopolymer blends including poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)/poly(vinyl phenol) [47], thermoplastic phenol formaldehyde resin/poly(ε-caprolactone) (PCL) [48], PHB/PCL [49], PLA/poly(butylene succinate) (PBS) [50], poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)/PLA [51], PHB/PLA [52], chitosan/soy protein [53], PHB/cellulose acetate butyrate [54], PLA/PEG [55], PHB/PBS [56], PLA/poly(epichlorohydrin-co-ethylene oxide) (PEEO) [57] and poly(propylene carbonate)/poly(ethylene-co-vinyl alcohol) [58].

2.4 Additives

Additives can range in distinctive variety, functionality, and use [12]. The specific purpose of using an additive in a biocomposite blend can be mechanical or barrier property retention at a variable cost [59], and the rationale to use a specific additive is dependent on the design criteria [60]. Additives for bioplastics range from impact modifiers, melt strength modifiers, heat resistance modifiers, coupling agents, lubricants, light stabilizers, colourants, flame retardants, foaming agents, odour reduction agent and biocides [60, 61].

Additives are compounded with polymer matrices through physical or chemical methods, which causes the molecular structure of polymer to be modified to accommodate the additive [59]. This intercalation permits uniform strengthening of the material as well as occupying the free volume available in the polymer.

2.5 Fillers

Fillers are often added to polymers to lower the overall cost, although fillers in some cases also modify the tensile and compressive strength, toughness, abrasion resistance, and dimensional and thermal stability [60].

2.5.1 Bio-based fillers

Bio-based materials are defined as “materials derived from renewable sources” [62], and used extensively in biocomposites as fillers [63]. According to ASTM: D7075-04, bio-based materials are the materials containing carbon based compound(s) in which the carbon is derived from contemporary (non-fossil) biological sources. Natural fibers are an abundant and renewable bio-based material [64], which are categorized as shown in *Figure 6* [65]. Natural fibers are crucial in achieving the specific requirements of the engineered biocomposites, and thus draw significant attention because of their greater potential over comparable fillers.

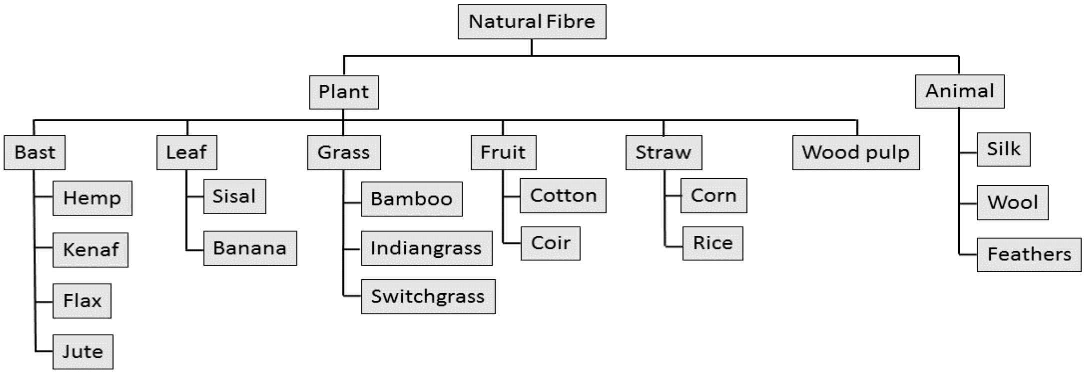

Figure 6. Classification of Natural Fibers [65]

A number of reviews about the properties of natural fibers and their use in polymeric composites can be found in the literature [66-70]. A majority of studies on natural fibers are concentrated around vegetal fibers and specifically on bast fibers such as flax, hemp, jute, and kenaf, which provide specific tensile strength comparable to E-glass fibers, and hence useful in re-engineering glass fiber reinforced composites with natural fibers. Natural fibers themselves can be considered as naturally occurring composites consisting of cellulose nanofibrils surrounded in a lignin matrix, thus affording tensional rigidity as they are aligned longitudinally [71]. Production of biodegradable composites by combining a bio-based polymer with low cost lignocellulosic natural fibers and fillers is becoming a very promising research direction in recent years that serve to (a) improve the mechanical/thermal stability, (b) to conserve biodegradability, and (c) enhance the cost-to-performance ratio [72].

Table 4 shows the chemical composition [73-79] and cost of key plant fibers and fillers used in biocomposites. The major constituents of lignocellulosic fibers and fillers are cellulose, hemicellulose, and lignin, where the composition can differ depending on the origin, species, age, and retting process.

Table 4. Chemical Composition of Key Natural Plant Fibers/Fillers [73-79]

Fiber/ Filler	α-Cellulose (wt. %)	Hemicellulose (wt. %)	Lignin (wt. %)	Extractive (wt. %)	Ash (wt. %)	Cost* (USD/kg)
Hemp	70.2-74.4	17.9-22.4	3.7-5.7	1.6	-	0.80-1.00
Bamboo	48.2	25.1	21.4	9.9	2.3	2.00-3.00
Banana	63.9	1.3	18.6	10.6	1.5	-
Coir	44.2	12.1	32.8	6.4	2.2	0.50-0.60
Cotton	90.0	6.0	-	0.4	-	0.50-2.50
Flax	64-74	11-17	2-3	1.5	-	1.00-1.70
Hardwood	31-64	25-40	14-34	0.1-7.7	<1	0.15-0.30
Hemp hurd	39-49	16-23	16-23	2-4	2-4	0.20-0.50
Jute	60-65	6-8	5-10	-	1.2	0.33-0.85
Kenaf	63.5	17.6	12.7	4.0	2.2	0.50-0.70
Pineapple	73.4	7.1	10.5	5.5	2.0	-
Ramie	68.6-76.2	13.1-16.7	0.6-0.7	6.4	-	3.00-5.00
Sisal	60-67	10-15	8-12	1.7-6.0	0.14-0.87	0.70-1.00
Softwood	30-60	20-30	21-37	0.2-8.5	<1	0.15-0.30

*obtained from Alibaba.com

Cellulose is considered the major framework component of the fiber structure, which provides strength, stiffness, and structural stability of the natural fiber. Cellulose is a non-branched polysaccharide constituted by cellobiose monomer, which consists of two glucose units covalently bound to each other by a glycosidic carbon (1-4)-linkage. The glycosidic linkage is β-configured that allows cellulose to form a flat and ribbon like long straight chain, which for wood fibers features lengths of 5 μm corresponding to a degree of polymerization (i.e., glucose units) of 10,000 [80]. The chemical structure of cellulose (*Figure 7*) consists of three hydroxyl groups (-OH). Two of these form intramolecular hydrogen bonds within the cellulose macromolecules whilst the rest of the group forms an intermolecular hydrogen bond with other cellulose molecules.

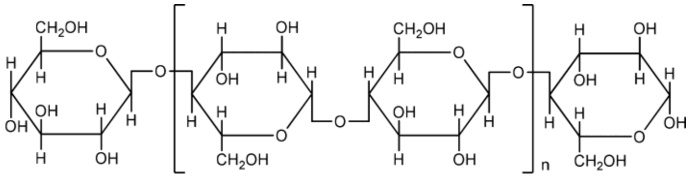

Figure 7. The chemical structure of cellulose showing the hydroxyl and key hydrogen bonds [81].

Hemicelluloses have lower molecular masses compared to polysaccharides, and are structurally the copolymers of glucose or xylose, glucuronic acid as well mannose. Hemicellulose can be degraded by both chemical and enzymatic hydrolysis. In contrast to cellulose, hemicelluloses are mostly branched molecules, and their degree of polymerization is 10–100 times lower. *Figure 8* shows a representative part of hemicellulose structure.

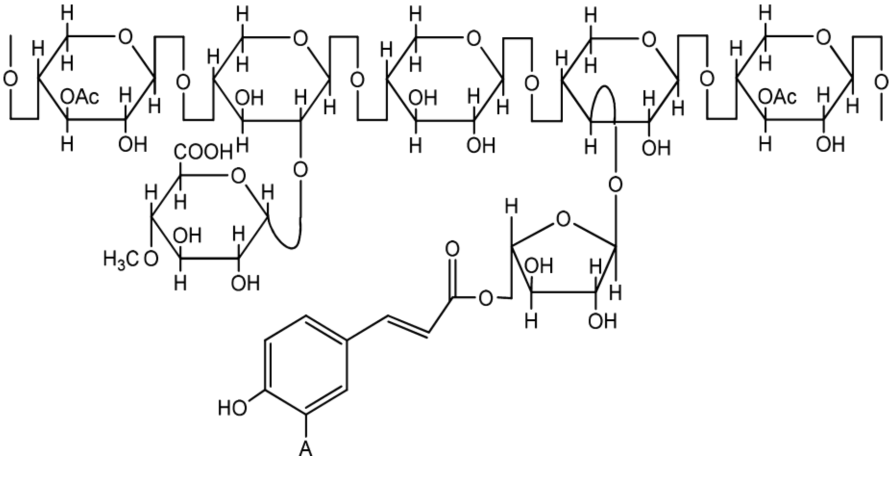

Figure 8. A representative part of the hemicellulose structure [81].

Lignin fills the space and acts as adhesive between the cellulosic fibers [82], produced during the irreversible removal of water from sugars, primarily xylose. As the plant develops, more lignin is produced, providing increased mechanical stability [83]. Lignin is resistant to most microorganisms, since its aromatic groups are resilient to anaerobic action, whereas its aerobic degradation is slow [81]. The exact structure of lignin remains unknown since it is insoluble in most solvents.

Plant fibers contain a fraction of pectin, which is the primary component of the middle lamella, as group of polysaccharides rich in galacturonic acid [84]. The exact structure of pectin is not entirely known, although the contended three main components are homogalacturan and ramnogalacturan I and II, covalently bonded on the primary cell wall and on the middle lamella, forming a complicated pectin network.

The exact structural organization of the chemical constituents in the cell wall understandably controversial, however, it is usually accepted that these three major polymers exist as separate entities (*Figure 9*) and are not homogenous. The hemicellulose polymers are believed to be bound to the cellulose microfibrils by hydrogen bonds creating a layer around the fibrils, and these cellulose/hemicellulose units are then encapsulated by lignin [85].

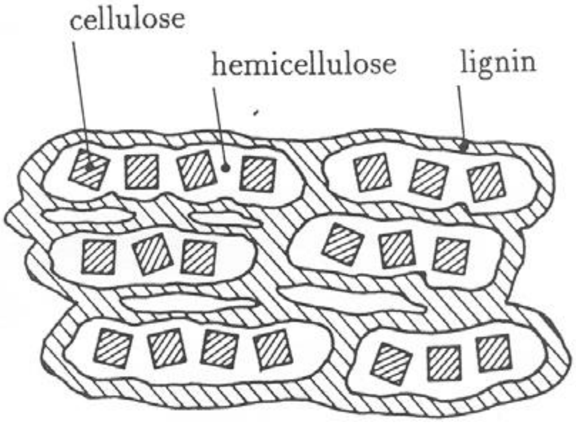

Figure 9. A model of the structural organization of the three major constituents in the cell wall of wood fibers [86]

A comparison of properties [70] of common natural and synthetic fibers is shown in *Table 5*. The chemical constituents and complex chemical structure affect the fiber properties.

Table 5. Properties of Selected Natural and Synthetic Fibers [70]

Fiber	Density (g/cm³)	Elongation (%)	Tensile strength (MPa)	Elastic modulus (GPa)
Cotton	1.5–1.6	7.0–8.0	400	5.5–12.6
Aramid (Std.)	1.40	3.3–3.7	3000–3150	63.0–67.0
Carbon (Std. PAN-based)	1.40	1.4–1.8	4000	230–240
Coir	1.20	30.00	593	4.0–6.0
E-glass	2.50	0.50	2000–3500	70
Flax	1.50	2.7–3.2	500–1500	28
Hemp	1.47	2–4	690	70
Jute	1.30	1.5–1.8	393–773	27
Kenaf	1.45	1.60	930	53
Ramie	-	3.6–3.8	400–938	61.4–128
S-glass	2.50	2.80	4570	86
Sisal	1.50	2.0–2.5	511–635	9.4–22
Softwood kraft pulp	1.50	4.40	1000	40

2.5.2 Nanofillers

Nanofillers are characterized by a nanometer size and a large surface area, leading to a high aspect ratio. Bio-nanocomposites utilize the large surface area of the nanofillers resulting in a large interfacial or boundary area between the matrix and nanofiller. This large interface enables the alteration of molecular mobility and the relaxation behavior besides mechanical, thermal, and barrier properties of the bio-nanocomposites [87]. Especially for food packaging applications, bio-nanocomposite materials are designed to have the ability to tolerate the mechanical and thermal stress during food processing, transportation, and storage [88].

Nanosized fillers can be either organic or inorganic such as clay (e.g., montmorillonite), natural biopolymers (e.g., chitosan), natural antimicrobial agents (e.g., nisin), metal (e.g., silver), and metal oxides (e.g., TiO_2) [89]. The incorporation of nanofillers may not only improve the mechanical, thermal, and barrier properties of the biopolymers but also offer other preferred functions and applications in food packaging such as antimicrobial action, biosensing, and oxygen scavenging.

2.6 Biocomposites

Biocomposites are made by combining natural fiber and petroleum derived non-biodegradable polymer or biodegradable polymers [69]. Biocomposites derived from natural fiber/filler and crop/bio-derived plastic are more eco-friendly, and such composites are named as green composites [71]. The majority of biocomposites are currently used in the automotive (door panels, seat backs, headliners, package trays, dashboards, and interior parts), construction, furniture, and packaging industries, where increasing environmental awareness and the reduction of fossil fuel resources are driving the development of new renewable products [43] for industrial products.

The combination of natural fibers/fillers with polymer matrices to produce biocomposites requires consideration of the fiber-matrix interface and processing methods. Published literature is mostly concentrated around starch-based and PLA-based biocomposites. The reader is directed to detailed discussions is available in published review papers on biocomposites based on starch, PHA, PLA, soy resin and wood plastics [66, 68, 90] for further research.

2.6.1 Biocomposite Compatibilizer and Plasticizer

Compatibilizer is an additive used to enhance the interfacial compatibility between the plastic and fillers. Poor interfacial adhesion, thermal degradability, moisture absorption and fiber agglomeration are associated with the incompatibility of the hydrophilic fibers and the hydrophobic thermoplastics [91]. The hydrophilic nature of lignocellulosic fibers/fillers is caused by the presence of hydroxyl groups (-OH) in the structure of the fibers. The crystalline cellulose is closely packed and most of its -OH positions are inaccessible because they are used for inter-chain bonding of the cellulose. On the other hand, non-cellulosic amorphous constituents (hemicellulose, pectin, lignin and waxes) are highly hydrophilic. Thus, chemically treating the fibers and effectively eliminating the hydroxyl linkages can improve hydrophobicity of natural fibers.

Chemical treatments can partially or completely remove non-cellulosic substances. However, other treatment methods using biological (retting), physical (steam explosion [92], plasma treatment [93] and mechanical (ball milling) [94]) have also been implemented in this regard as well. All these methods aim to eliminate the cementing non-cellulosic materials and/or increase the roughness of the fiber surface. The elimination of cementing materials causes reduction of hydrophilicity and increase in the crystallinity of fibers, and as a result, improves interfacial bonding of fibers and matrix and furthermore increases the fiber surface roughness that aids in the interlocking of fibers and the matrix.

A plasticizer is used to improve flexibility, ductility, and toughness of polymers while reducing hardness and stiffness [95]. Plasticizers work by decreasing the strength and amount of the intermolecular forces in the material [96]. These additives are usually liquids with low molecular weights and low vapor pressures.

2.6.2 Modification of natural fibers

A fiber surface modification is often required to address the incompatibility of natural fibers/fillers with polymer resins during processing. Surface modification includes (a) chemical methods such as mercerization, acetylation, and silanization, (b) physico-chemical methods such as solvent extraction, (c) physical methods such as the impingement of plasma or application of steam, and (d) pure mechanical methods such as rolling or swaging [90]. While most of the surface treatments are performed before processing, chemical methods of fiber surface treatments can be applied during processing. The reader is encouraged to additional reading on review of these surface treatments on natural fibers by Kabir et al. [97]. *Table 6* shows a comparison of common surface modification methods of natural fibres for composites

Table 6. Common Surface Treatment of Natural Fibres

Method	**Benefit**	**Shortcoming**
Physical Method	• No change on the chemical composition but modify the surface properties • Good mechanical bonding with the matrix and enhance composite properties	• Less effective than chemical treatment

Alkaline Treatment	• Increase surface roughness resulting in better mechanical interlocking • Remove a certain amount of lignin, wax and oils • Increase the amount of cellulose exposed on the fibre surface, thus increasing the number of possible reaction sites • Improve mechanical, impact fatigue and dynamic mechanical behaviours of fibre-reinforced composites	• At higher alkali concentration, excess delignification of natural fibre occurs resulting in a weaker or damaged fibre • The tensile strength of the composite decrease drastically after certain optimum NaOH concentration
Silane Treatment	• Reduce the number of hydroxyl groups in the fibre matrix interface • Restrain the swelling of the fibre by creating crosslinked network due to covalent bonding between the matrix and the fibre • Effective in modifying natural fibre-polymer matrix interface and increasing the interface strength • Stronger fibre-matrix than that of alkaline treatment • Improve thermal stability	
Acetylation	• Reduce the hygroscopic nature of natural fibre and increase the dimensional stability • Hydroxyl groups of the cell wall with acetyl groups become hydrophobic • Higher bio-resistance and less tensile strength loss compared to silane treated fibre in biological test	
Benzoylation Treatment	• Decrease hydrophilic nature of the treated fibre and improve interaction with hydrophobic polymer matrix • Increase strength of composite, decrease its water absorption, and improves its thermal stability	• Requires pre-treatment with alkaline to activate the hydroxyl groups of the cellulose
Acrylation and Acrylonitrile Grafting	• Reduce the affinity of fibres to moisture	• Application of excessive amount of Acrylonitrile reduces tensile properties
Maleated Coupling Agents	• Improve interfacial bonding and mechanical properties of the composite	

Physical methods of surface treatment include stretching, calendaring, thermos-treatment, and the production of hybrid yarns for the alteration of natural fibers. Physical methods involve treatment by corona-discharge treatment [98], physico-chemical treatment, such as steam explosion treatment [99], high energy ray radiation processing [100] or plasma treatment [101], and autoclave treatment [102]. The aforementioned physical methods aim to enhance the fiber-matrix adhesion by reducing the difference between hydrophilic/hydrophobic characters of fiber and the matrix [98]. Physical treatments change structural and surface properties of the fiber, and further influence the mechanical bonding of polymers. Chemical composition of the fibers is not extensively altered because of physical treatments, albeit effectively, the interface is enhanced through an increased mechanical bonding between the fiber and the matrix.

Chemical modifications of natural fibers aimed at improving the adhesion within the polymer matrix using different chemicals are extensively investigated. Most of the chemical modifications of natural fiber involve silanization [103], alkalization (mercerization) [104], acetylation [105], cyano-ethylation [106], benzoylation [107], isocyanate treatment [108], dewaxing [109], enzyme treatment [110], esterification [63], etherification [111], and graft copolymerization [107, 112]. Other modifications of natural fibers include crosslinking with formaldehyde, p-phenylenediamine and phthalic anhydride; nitration; dinitrophenylation and transesterification [113, 114].

3 Challenges with Current Food Packaging Materials

Current food packaging solutions grapple with issues even through current practices are largely effective, including challenges in the materials used and their possible interactions with food, especially when food packaging plastics are reused [8, 12]. In addition, the common disposal methods of food plastics as well as poor recycling policies and results will continue to further deteriorate the environment if solutions are not found [8].

3.1 Material-Food Interactions

Food and packaging interactions are the interplay between food, packaging, and the environment with an effect on the food and/or packaging [115]. It is understood that a divergent range of chemicals can be detected in foodstuff as they progress in the supply chain including variable amounts of additives, pesticides, contaminants, mycotoxins, and micronutrients [116]. When food packaging comes in direct contact with foods, they act as a source of chemicals in a phenomenon termed as ‘migration’ [117].

Migration can be categorized as three different types dependent on the food systems examined: (1) non-migrating system, (2) volatile system, and (3) leaching system [116]. Non-migrating systems feature a miniscule transport of high molecular weight polymers, and inorganic chemicals. A volatile system operates without a physical contact between food and packaging and is pertinent to dry foodstuff exhibiting low contact potential with packaging. In a volatile system, the migrant diffuses or evaporates, or is desorbed and adsorbed on to the product. A leaching system operates through food/package contact, and the migration occurs through diffusion and subsequent dissolution and dispersion into foodstuff, and pertinent to liquid foodstuff packaging or wet solid products [118].

Migration is affected by the nature of the food [119], the type of contact [120], the time of contact [121], the temperature of contact [122], and the nature of the packaging material [116], all of which bear a direct influence over its extent and rate. Due to the extremely complex chemical and physical structure of foods, migration tests are usually performed using food simulants. The most recent EU regulation 10/2011 [123] for plastics packaging materials refers to three categories of food simulants, except for water and addition of different concentrations of ethanolic solution, i.e., (1) acetic acid (3 %v/v), (2) ethanol (10, 20 and 50 %v/v), and (3) vegetable oil.

The degree of migration is determined by measuring the rate of migration of a specific chemical compound or element from packaging material to food. Chromatographic techniques and plasmatographic analysis such as spectroscopy (IR), gas chromatography (GC), gas chromatography–mass spectroscopy (GC-MS), liquid chromatography (LC), liquid chromatography-mass spectroscopy (LC-MS), inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) [124] are extensively used for this purpose. Furthermore, in some cases, solid-phase extraction, liquid-phase extraction, supercritical fluid extraction and head space-sorptive extraction are applied in combination with IR, GC, GC-MS, LC and LC-MS [118].

The migration of chemicals and elements from packaging plastics into foodstuff is tolerated to a certain level as specified by the guidelines put forth by regulatory agencies. Materials selection for biodegradable plastics for food packaging hence requires consideration of the overall migration of such substances into food simulants being maintained at acceptable levels.

3.2 Disposal of Food Packaging Materials

Many existing food packaging plastics of petrochemical origin are not biodegradable, leading to billions of tons of plastics being landfilled, which causes a strain on resources as well as the environment because of leaching and a lack of volume control [125]. This challenge is synonymous with the discharge of chemicals through agricultural runoff into the Australian Coral Sea, leading to the bleaching of the Great Barrier Reef [126]. Currently, there is a lack of an economically sensible method to approach this migration issue. A reduction in plastic use or material modification towards higher biodegradability is advocated to deescalate this overwhelming challenge.

3.3 Cost of Food Plastic Polymers

The food industry spends approximately $84 billion a year on food packaging and processing in the United States alone [8]. Of the total food cost, approximately 8% of the price to the consumer is spent on food packaging and processing. Therefore, it is advantageous to both the consumer and the food industry to use functional and cost effective food packaging techniques and materials. Petroleum-based plastics have become the dominant form of food plastics because of their relatively inexpensive prices and high availability. These aspects hinder the bioplastic growth and acceptance in the food packaging market since the manufacturing processes are relatively expensive and in their infancy, when compared to their petrochemical counterparts. However, without the development of low-environmental-impact packaging materials or more efficient recycling programs, the continual use of petrochemical polymers for food packaging may have a tremendous ecological and economical effect.

3.4 Antibacterial Food Packaging

In recent years, new food packaging systems have been developed as the response to trends in consumer preferences towards mildly preserved, and convenient food products with a prolonged shelf-life [127]. In addition, food-borne microbial outbreaks are driving an exploration for innovative means to inhibit microbial growth in the foods while preserving quality, freshness, and safety [128]. Traditional systems are reaching their limits with regard to further extension of shelf-life of packaged food. To offer further shelf-life extension and to improve the quality, safety and reliability of the packaged food, innovative packaging concepts are being developed. Examples of these are incorporating oxygen, moisture, and ethylene scavengers, the use of carbon dioxide or ethylene emitters in other foods, flavor imparting or scavenging chemicals, and antimicrobial agents for microbiological safety of food [23]. The application of antimicrobial agents to packaging can create an environment inside the package that may delay or even prevent the growth of microorganisms on the product surface and, henceforth, lead to an extension of the shelf life and/or the enhanced safety of the product, as shown in *Figure 10*. Antimicrobial packaging is a form of active packaging that interacts with the product or the headspace between the package and the food system, to achieve the aforementioned goals [128].

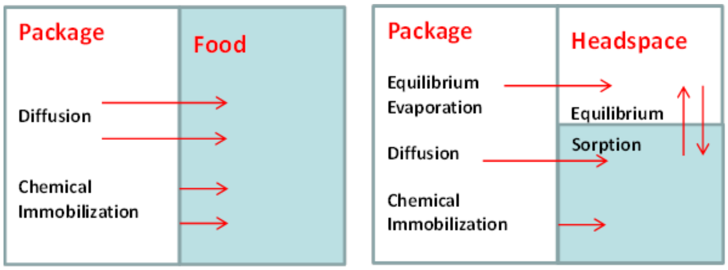

Figure 10. Food packaging systems and migration phenomena [129]

Antimicrobial packaging can take several forms [128] with the antimicrobial agents constituted as:

1. Volatiles in sachets/padded packages
2. Volatiles and non-volatiles in polymers
3. Coating or adsorbent on polymer surfaces
4. Covalently bonded to polymers through
5. Polymers with antibacterial action

Food packaging with antimicrobial activity can be divided into two groups; (1) packages that allow the antimicrobial to migrate into the food, and (2) packages that do not release antimicrobial substances and inhibit microbial growth on the food surface [130]. In the first case, a preservative is found either within the matrix or on the surface of the food-packaging material. The corresponding substance can be released completely or in dosed amounts on the food surface to perform the biocide action. *Figure 11* shows a schematic representation for the first case in which (A) represents a packaging system that incorporates the antimicrobial agent in a single layer and releases it gradually into the food matrix, (B) represents the same concept but with an inner layer, which can be useful in controlling the release of the antimicrobial compound. (C) consists of a layer of food-packaging material coated with a formulation containing an antimicrobial substance [9, 28]. In the second case, as it is shown in *Figure 11*, the scheme (D) represents a packaging system in which antimicrobial activity occurs only when microorganisms contact with the surface of the packaging material [131-133].

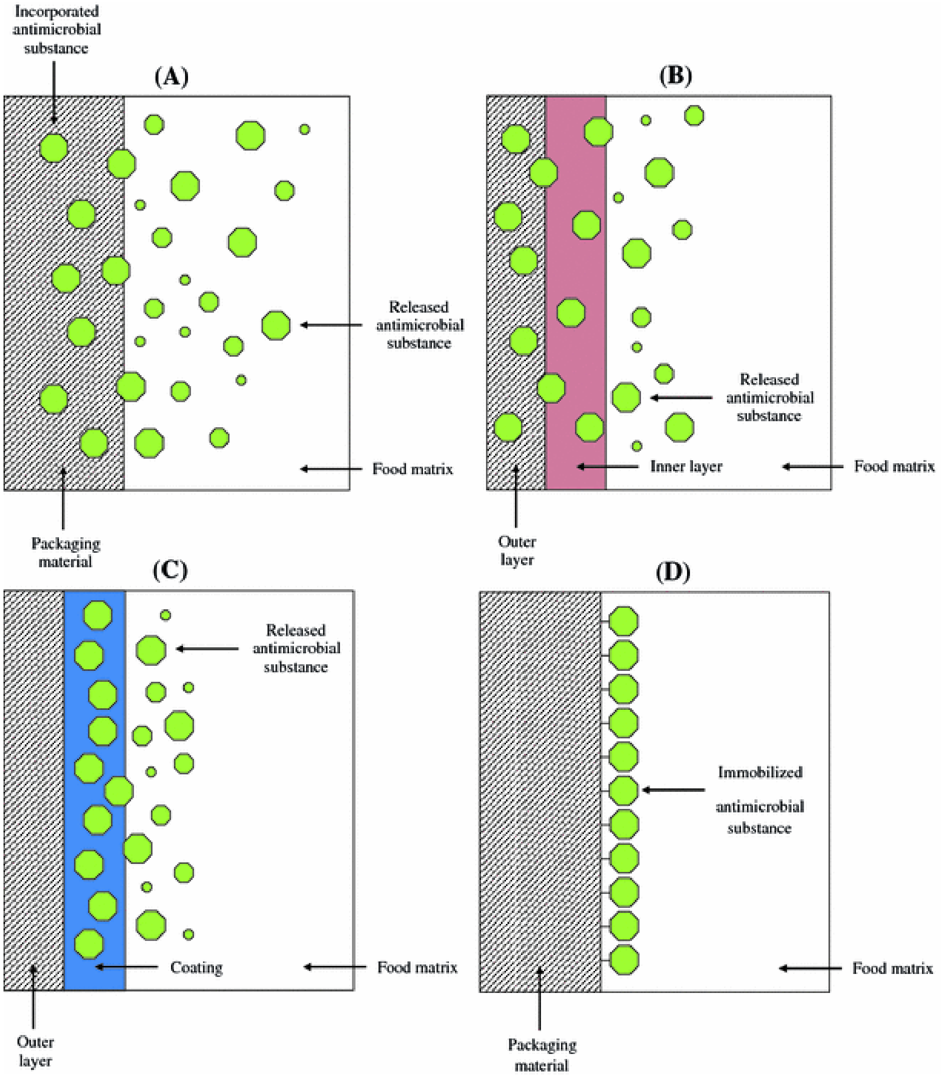

Figure 11. Antimicrobial food-packaging systems [131-133].

4 Design and manufacturing

4.1 Defining properties and eco-design

The type of foodstuff to be contained by packaging dictates packaging requirements. A food package (*Figure 12*) should hinder gain or loss of moisture, prevent microbial contamination and act as a barrier against permeation of water vapor, oxygen, carbon dioxide and other volatile compounds such as flavors and taints, in addition to the basic properties of packaging materials such as mechanical, optical, and thermal properties [88].

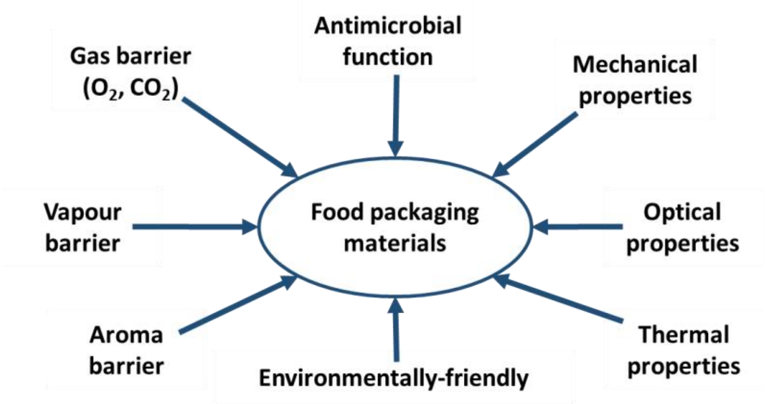

Figure 12. General properties required for food packaging materials [88].

Many factors can affect the performance of biocomposites. In addition to the individual properties of the biocomposite constituents (fiber/filler and matrix), the performance of the biocomposites is also influenced by fiber/filler content, fiber/matrix interfacial interaction. Furthermore, processing and manufacturing conditions and associated variables in composites production are also critical. The selection of appropriate processing techniques leads to optimum biocomposite performance, and specifically demonstrated through the tensile, flexural, impact, damping and vibration properties of the biocomposites.

Specific business benefits of eco-design for packaging with some principles are listed by Hollaway et al. [134] , such as greater resource efficiency (materials, energy and labor), added functionality and effectiveness, better product differentiation in overcrowded markets, reduced environmental impact during use and disposal, and opportunity for innovation in new product forms. These principles are reflected in an eco-design wheel (*Figure 13*), which can be easily adapted for use in packaging design.

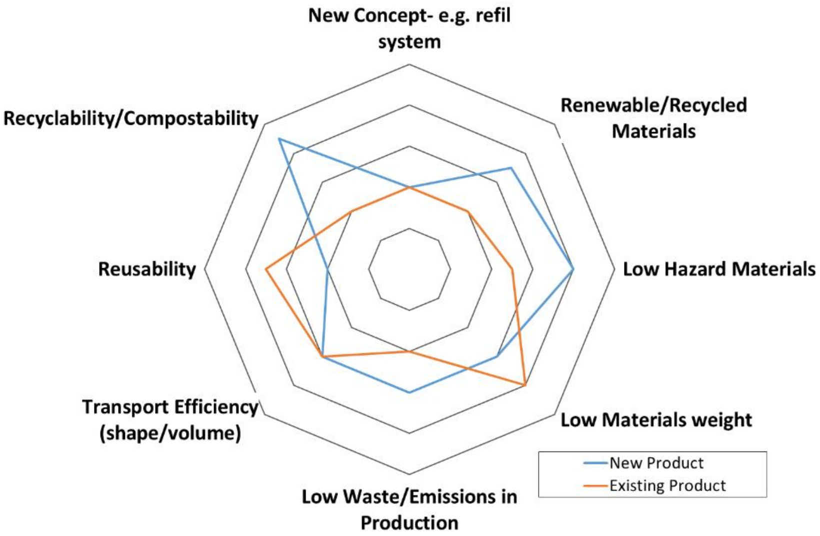

Figure 13. A plot of criteria in food packaging defining the Eco-Design Wheel [134].

The application-specific selection of the optimal processing method and related control parameters is a challenge for biocomposites in addition to the inherent variability shown by natural fibers/fillers when designing biocomposites.

4.2 Material Selection

Materials selection is a fundamental part of the product design and development process. To manufacture products that efficiently perform their function in specified operating conditions over their design life, appropriate material selection is necessary. The selection process is dictated by component function, objectives, and technical and financial constraints. In addition to selecting viable materials for commercial applications, the shape determines the processability and manufacturability, with constancy in component quality is of paramount importance. The selection of materials for a given component may be a relatively perplexing because of the possible large variety of materials and related manufacturing processes available. Contemporary materials selection techniques often rely on a large data bank of materials and their properties [135-137].

4.2.1 Fibers/Fillers

The selection of bio-derived plant fibers and fillers for efficient product design and development entails closing the existing gap between current scientific knowledge and actual market applications, with Ashby-type materials screening charts of particular importance as useful visual tools. *Figure 14* shows a comparison of absolute tensile properties, tensile properties per unit density, tensile properties per unit cost, and tensile properties per unit eco-impact, for various categories of plant fibers [135].

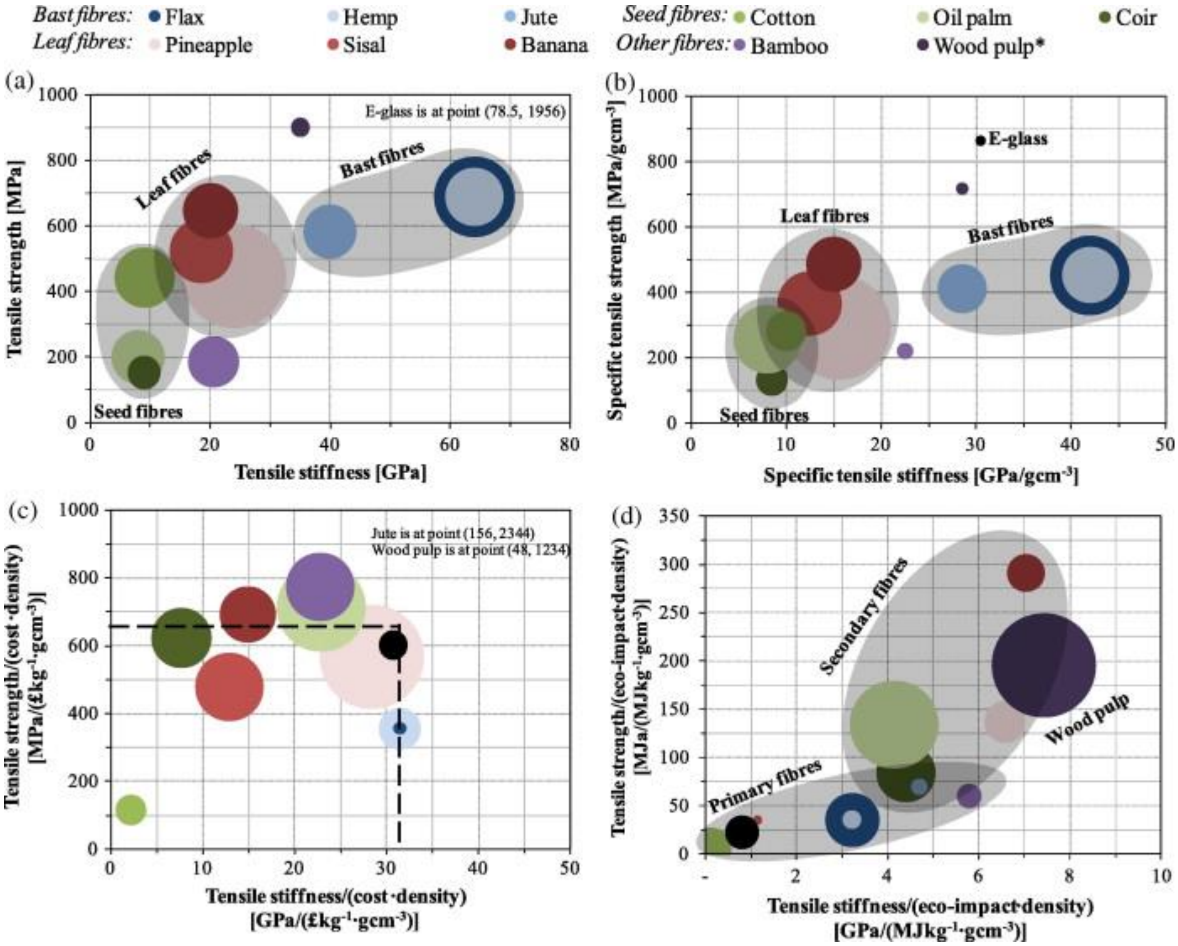

Figure 14. Charts comparing the (a) absolute tensile properties, (b) tensile properties per unit density, (c) tensile properties per unit cost, and (d) tensile properties per unit eco-impact, for various categories of plant fibers. Bast fibers are a shade of blue, seed fibers are a shade of green, leaf fibers are a shade of red [135].

In terms of absolute tensile properties, bast fibers show high strength (up to 700 MPa) and stiffness (up to 70 GPa) where ramie, flax, and hemp exhibit higher properties than jute and kenaf [138]. Leaf fibers tend to have moderate to high strength (300–700 MPa), but lower stiffness (10–30 GPa) in comparison to bast fibers. Seed fibers, in contrast, have low to moderate strength (100–500 MPa) and low stiffness (up to 15 GPa).

Plant fibers excel in specific mechanical properties; however, without a decrease in cost over their counterparts, they cannot be economically viable. Seed and leaf fibers offer high tensile strength per unit cost, and bast fibers offer high tensile stiffness per unit cost. The cost of natural fibers and fillers varies depending on the place of origin and local economy. Since plant co-products avoid the use of new agricultural lands and do not compete with food sources, their utilization is lucrative from both economic and environmental standpoints [139], as they also provide a monetary source if used in a value-added product.

The moisture content at a given relative humidity can affect the performance of a composite made from natural fibers, and hence fiber drying before processing is an important step [66] in manufacturing. Moisture content of natural fibers/fillers vary with relative humidity [140] because of their constituents (such as cellulose, hemicellulose and lignin). The enhanced water content can significantly affect the compression, flexural and tensile properties of the composites [73], where fiber surface treatments assist in decreasing the moisture content level and the rate of moisture absorption.

4.2.2 Bioplastics

The selection of bioplastics for design and manufacturing analysis is constricted to a spectrum of biopolymers including starch, PLA, and Polyhydroxyalkanoates (PHA). Among these biopolymers, starch and PLA biopolymers are valuable for food packaging since they have become commercially available, possess a balance of properties, and are produced at an industrial scale [141].

Since lactic acid exist as two optical isomers, l- and d-lactic acid, three different stereo-chemical compositions of lactide are available, i.e., l,l-lactide, d,d-lactide and l,d-lactide. This stereo-chemical composition determines the resultant properties of the polymer. The processing possibilities of this transparent material are very wide, ranging from injection molding and extrusion over cast film extrusion, to blow molding and thermoforming [7, 142]. However, brittleness, thermal instability, low melt strength, high water vapor, and oxygen permeability restrict the use of PLA films for many food packaging applications [44]. Whereas its high stiffness can be reduced by the addition of plasticizers, these additives also lead to a reduction in oxygen barrier and thermal resistance [141]. This effect is one of the contemporary challenges in the development of biocomposites with PLA for food packaging applications.

More than 100 PHAs are known, of which poly(hydroxy butyrate) (PHB) is the most common. The PHAs bear the potential as a substitute for many conventional polymers, since they retain high water barrier properties [143]. However, these materials are relatively expensive, leading to challenging competition with conventional thermoplastics. Therefore, the addition of bio-based fillers gathers clear practical interest, specifically in lowering cost.

High-water content or plasticizers (glycerol, sorbitol) are necessary to produce a plastic-like starch-based film. These plasticized materials (application of thermal and mechanical energy) are called thermoplastic starch (TPS) and constitute an alternative for polystyrene (PS). Starch-based thermoplastic materials, e.g., blends of TPS with synthetic/biodegradable polymer components, like polycaprolactone, polyethylene-vinyl alcohol or polyvinyl alcohol are effectively applied on industrial level for foaming, film blowing, injection molding, blow molding and extrusion applications [40].

Cellulose esters such as cellulose (di)acetate and cellulose (tri)acetate require additives to manufacture thermoplastics. Injection molding or extrusion can process most of them. Cellulose ethers such as hydroxypropyl cellulose and methylcellulose are water-soluble, except for ethyl cellulose and benzyl cellulose. Ethyl cellulose can be used for extrusion, laminating or molding after addition of plasticizers or other polymers. Most of these derivatives show excellent film-forming properties, but are too expensive for bulk use [143].

Because of the hydrophilic nature of starch and cellulose, packaging materials based on these materials have a low water vapor barrier, which causes a limited long-term stability and poor mechanical properties, which are also sensitive to moisture content. The alternating hydroxyl side chains along the cellulose backbone are responsible for the poor moisture-barrier properties of cellulose-based packaging materials. They also contribute to the highly crystalline structure of cellulose which, in turn, results in a packaging material that is brittle and demonstrates poor flexibility and tensile strength. Thus, other drawbacks are inadequate processability, brittleness and vulnerability to degradation [44].

4.3 Processing Methods

The natural fiber type and content is essential for furthering the sustainability of the composite. In addition, natural fiber/filler aspect ratio (length/diameter), chemical composition hold an effect on the processing, and therefore processing parameters and physical accessories should be well planned in case of commercialization [66], as the appropriate selection of processing method is critical.

Extrusion, baking, thermoforming, casting, blow molding, injection molding, lamination, calendaring and coating are major plastic processing methods that are currently applied by the plastic industry in producing food packaging [144]. With few exceptions, bio-based polymers exhibit a great deal of adaptability for many of these plastic processing methods requiring little or no re-engineering [145, 146]. Table *7* shows a comparison of some common biocomposites manufacturing processes.

Table 7. Benefits and shortcomings of common biocomposites manufacturing processes

Process	**Benefit**	**Shortcoming**
Extrusion	Twin screw extruder is very effective mixing devices for compounding blends and composites	Not suitable for long fibre
Compression Moulding	Less damage on fibre compared to extrusion and injection moulding	Time consuming process
Injection Moulding	Injection moulding is suitable only for short fibres.	During injection moulding, extensive fibre damage occurs due to the intensive mixing with

		high-shear and passage through a narrow gate.
Solution Mixing	The solution mixing procedure avoids fibre damage that normally occurs during blending of fibre and thermoplastic by melt mixing	This process requires solvent which had made it expensive and slower than slower than other techniques.

Biocomposites can be produced using similar methods as fiber reinforced thermoplastic composites. Reported works on natural fibers/PLA biocomposites are shown in *Table 8*. The most common methods for manufacturing natural fiber reinforced thermoplastics are compression and injection molding. Also, melt mixing, solution mixing, and extrusion are common for producing mixtures (granules) of bio-based fillers and thermoplastics. Each processing method has its own advantages and limitations. Compression molding and infusion processes (resin transfer molding and vacuum infusion) produce plastic composites with similar specific tensile properties. Despite the use of aligned reinforcements, hand lay-up produces composites with only moderate mechanical properties [147].

Table 8. Key Reported Works on Natural Fibers/PLA Biocomposites

Natural Fiber/filler	**Fabrication technique**	**References**
Flax	Twin-screw extruder, compression molding; Carding machine, hydraulic press, shredder, injection molding; Stack of polymer films and fiber mats by hot press; Solvent casting, hot press Needle punched nonwoven (fibers), solvent casting	[24, 28, 148-150]
Kenaf	Solvent casting; Melt mixing, compression molding; Compression molding; Prepregs, hot press; Hot press (fiber and PLA film); Hot press (fabric and PLA film); Twin-screw extruder, injection molding; Single screw machine; hot press; Twin-screw extruder, injection molding; Twin-screw extruder, injection molding;	[151-161]
Hemp	Hot press (fiber and PLA film); Melt mixing, hot press; Twin-screw extruder, injection molding; Twin-screw extruder, injection molding; Compression molding; Twin-screw extruder, injection molding;	[25, 162-168]

Natural Fiber/filler	Fabrication technique	References
	Compression molding (film stacking); Hot press (woven fabrics and PLA sheets);	
Jute	Compression molding; Hot press (jute mats and PLA film); Micro-braid yarn with jute and PLA, compression molding; Compression molding; Extruder and injection molding;	[153, 169-172]
Abaca	Extruder and injection molding Melt mixing and injection molding Two-step extrusion coating process, injection molding	[172-174]
Bamboo	Mixing, filtering and compression molding; Compression molding; Twin-screw extruder, injection molding; Hot press;	[175-178]
Man-made Cellulose	Carding machine, hydraulic press, injection molding; Extruder and injection molding; Two-step extrusion coating process, injection molding; Twin-screw extruder, injection molding;	[148, 172, 174, 179]
Henequen	Compression molding;	[153]
Recycled newspaper cellulose fiber	Micro compounding (single-screw extruder), injection molding;	[180]
Wood	Melt mixing, hot press; Extrusion and injection molding; Twin-screw extruder, injection molding;	[171, 181, 182]
Sugar beet pulp	Blender and hot press; Extrusion and injection molding;	[183, 184]
Silk	Extrusion and injection molding;	[185]
Microcrystalline cellulose (MCC)	Twin-screw extruder, injection molding;	[186]
Rice Husk, Rice Straw, Banana fiber	Extrusion and injection molding; Internal mixing and compression molding; Melt mixing and hot press;	[159, 187, 188]
Ramie, Sisal, Coconut	Hot press; Blended using a two-roll plastics mill followed by hot press; Compression molding; Melt mixing and compression molding; Hot press;	[189-194]

The composite manufacturing technique is interconnected with three key composite parameters; (i) volumetric composition (maximum achievable fiber volume fraction and porosity), (ii) reinforcement form and (iii) matrix type [147]. Suitable manufacturing processes transform the materials to the final shape without causing any defect of products. For the selection a suitable process to manufacture biodegradable polymer composites, design and manufacturing engineers focus on multiple criteria including desired properties, size and shape of resultant composites, processing characteristics of raw materials, the production speed and the manufacturing cost [195].

5 Properties

The performance of a composite material is determined by its properties and behavior under tensile, flexural, compressive, shear and other static or dynamic loading conditions. Composites properties can be evaluated by conducting standard mechanical and physical tests under monitored laboratory conditions.

5.1 Moisture absorption

The moisture absorption by biocomposites containing natural fibers/fillers affects the properties and thus affects their long-term performance. For example, increased moisture decreases their mechanical properties [196, 197], creates the necessary condition for biodegradation, and causes dimensional instabilities [198]. Coupling agents, compatibilizers or other chemical modifications are used to improve the moisture resistance of biocomposites [199, 200]. However, moisture absorption of composites is still one a key challenge especially for their outdoor applications. The increase in water absorption and specimen dimensions of starch-filled PLA composites because of swelling [201] is proportional with increasing starch content (*Figure 15*). Thus, moisture absorption increases with increasing fiber/filler loading in the biocomposite [202]. Lignocellulosic natural fibers/fillers with less hemicellulose and more lignin showed less water uptake [203] since hemicellulose is highly hydrophilic where lignin is hydrophobic.

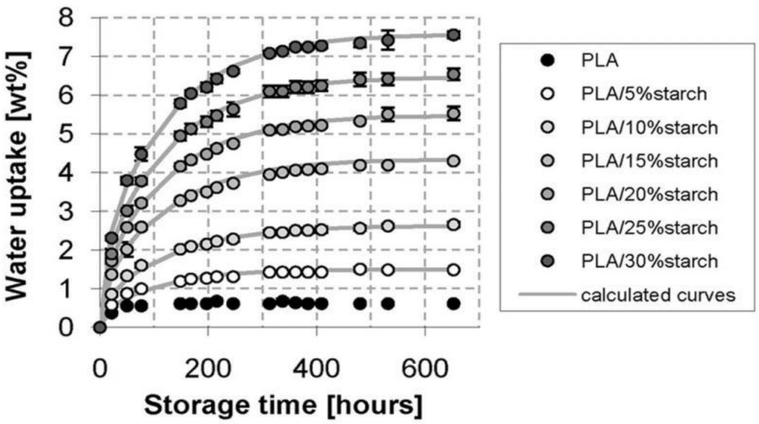

Figure 15. Measured and calculated water absorption of starch-filled PLA specimens as a function of storage time [201]

Mercerization or alkali treatment improves the adhesive characteristics of fiber surface and alkali treatment leads to fibrillation providing large surface area, and hence a better mechanical interlocking between fiber and matrix causing less water absorption [203] is realized. Besides, the treatment with NaOH solution promotes activation of hydroxyl groups of the cellulose by breaking the hydrogen bonds. Among amino silane and vinyl silane treatments given to the fibers, the higher water uptake was exhibited upon vinyl silane treatment [69]. This is due to better interaction between the amino silanes in composites resulting higher resistance to water.

Grafted copolymers also improve water resistance of biocomposites, for instance, at the same starch content, the acrylic acid grafted PLA/starch blend exhibited higher water resistance in comparison to the PLA/starch blend [204], where interaction of the AA-grafted-PLA with starch increased the hydrophobicity of the starch in the blend.

5.2 Thermal stability

During processing of biocomposites, natural fibers/fillers are exposed to high temperature, often combined with trapped air, which might cause thermal degradation. Fiber degradation at melt temperatures can diminish the reinforcement effect and also cause discoloration and odor in biocomposites [205]. Thermo-gravimetric analysis (TGA) is used to determine the high temperature degradation behavior of the composites as well as their components under air and nitrogen atmospheres.

Thermal degradation behavior is influenced by alteration of natural fibers/fillers or improvement of interfacial bonding between matrix and fibers, fiber content in the biocomposites, moisture content and any other additives incorporated [205]. A typical TGA curve of hemp hurd/PLA biocompoistes is shown in *Figure 16*. The initial 6 - 8% of weight loss can be attributed to the residual moisture in the fiber [206]. Then, the second stage of degradation involves the degradation of hemicellulose, lignin, and cellulose [207]. These temperatures are in a similar range as analyzed [208] for wood, hemicellulose, cellulose and lignin. Hemicellulose is the least thermally-stable compound, which degrades around 300°C. Lignin degradation begins around 300°C, and finishes around 450°C. Cellulose degradation starts at 275°C, and is found to completely degrade at around 550°C [208]. Therefore, in all of the TGA curves of biocomposites, two main degradation regions can be observed. The first region is caused by the thermal degradation of cellulose, hemicellulose, and lignin in the hemp hurd [209], and the second higher temperature region is attributed to depolymerization of the PLA [210].

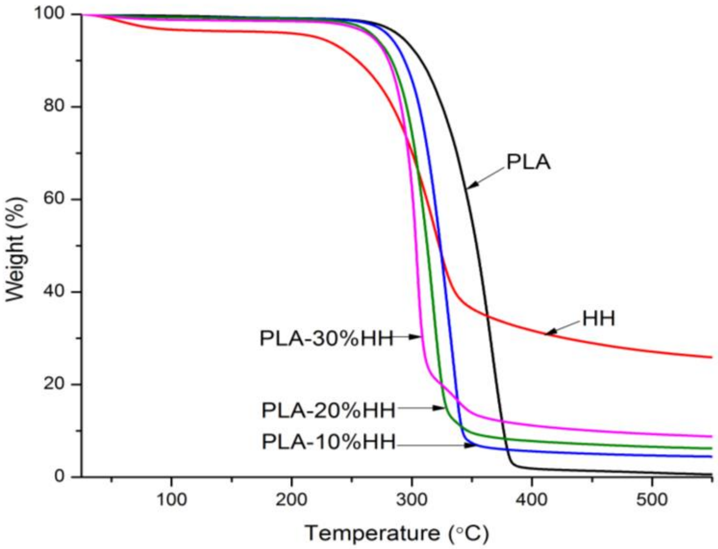

Figure 16. TGA curves of the neat PLA and hemp hurd/PLA biocomposites

The thermal degradation of the fibers also results in production of volatiles (at processing temperatures > 200ºC) that can lead to porous polymer products with lower densities and inferior mechanical properties [211].

5.3 Mechanical properties

The mechanical properties in tension, flexure, and creep are critical and defining for natural fibers used in biocompsites. Natural fibers are suitable for reinforcing bioplastics, due to their relatively high strength, stiffness, and low density compared to conventional fibers such as E-glass.

For biocomposites, the tensile test is the primary benchmarking method. The fiber strength is an important factor in the application-specific selection of a natural fiber. Whereas the tensile testing is representative of the through thickness property, the flexural testing is dependent on the outer and inner faces of the material [66]. The tensile properties of natural fiber reinforced composites are comparable with conventional fibers such as glass, carbon in reinforcing plastic materials. However, a major challenge of utilizing natural fibers as reinforcement in bioplastics is the incompatibility that results in poor adhesion between natural fibers and polymer matrix, consequently leads to low tensile properties [70]. In order to improve fiber–matrix interfacial bonding and enhance tensile properties of the composites, novel processing techniques, chemical and physical modification methods are developed.

The mechanical properties of the PLA and its biocomposites with bamboo cellulose fiber (BCF) were investigated [212]. With the addition of virgin BCFs, the Young's modulus was increased slightly because of the high stiffness of the BCF itself. While the ultimate tensile strength, the elongation at break, as well as the impact toughness were decreased noticeably, this was mostly attributed to the inadequate dispersion of BCF and poor interfacial interaction between the filler and matrix. Since the mechanical properties of the biocomposites decreased with the filling of the virgin BCFs, the necessity of the surface modifications of BCF was realized. The authors carried out three kinds of pre-treatments (5 wt. % NaOH aqueous solution, silane coupling agent KH560 and maleic anhydride) that caused significant improvements in the mechanical properties of the biocomposites compared with PLA reinforced by untreated BCFs. The increases in Young's modulus, tensile strength, elongation at break and impact toughness were found after each of the modifications. From the investigation, it was found that the cellulose pretreated with 5 wt. % NaOH provided the PLA composites with higher strength, and KH560 coupling achieved best toughness. Particularly, MA grafting PLA displayed moderate effects on improving both strength and toughness. Similar observation have been reported elsewhere in the literature, for instance, tensile strength significantly increased in bamboo flour filled polylactic acid (PLA) composites [213, 214] where glycidyl methacrylate (GMA) was used as coupling agent.

The addition of alkali and/or silane treated kenaf fibers in PLA matrix through compression molding using the film-stacking method with a fiber content of 40 wt. % were studied [82]. Although the introduction of treated kenaf fibers significantly improves, the flexural modulus compared to the neat PLA matrix, the flexural strength of the PLA composites decreases with the addition of kenaf fibers. The composite with silane-treated fibers showed an increase of 69% in modulus than that of alkali treated fibers. A carding process was used [215] that provided a uniform blend of PLA fiber and kenaf fiber that was followed by needle punching, pre-pressing and further hot-pressing in presence of silane coupling agent to form the biocomposite material. The flexural modulus and flexural strength of the treated fiber biocomposites increased with respect to neat PLA and untreated fiber biocomposites.

Impact strength is influenced by the processing factors more than other mechanical properties. This could be due to the phase separation of the components in the multiphase material [216]. The impact strength of short fiber composites are largely influenced by matrix intrinsic properties, optimum fiber–matrix interaction, fiber concentration, fiber geometry, fiber–matrix stress transfer efficiency, fiber orientation, fiber dispersion and distribution [217]. Biocomposites of PHBV with wood and bamboo fibers were fabricated using extrusion followed by injection molding. Tensile and flexural modulus increased with fiber loading for biocomposites with the two kinds of fiber and no considerable difference among the two fiber loadings (30 and 40 wt. % fiber) was noticed. However, notched impact strength of PHBV decreased with the fiber addition and the reduction was greater in case of bamboo fiber biocomposites [218]. The influence of processing parameter on miscanthus reinforced PBS/PBAT (60/40 wt. %) composites was investigated [216]. The temperature and fiber length were observed to have a significant effect on impact strength. On the other hand, holding pressure did not show any effect on the response when varying its levels.

5.4 Barrier properties

The determination of the barrier properties of a polymer is crucial to estimate and predict the shelf life of the product-package. The specific barrier requirement of the package system is related to the product characteristics and the intended end-use application. In general, plastics are relatively permeable to small molecules such as gases, water vapor, organic vapors, and liquids and they provide a broad range of mass transfer characteristics, ranging from excellent to low barrier value, which is important in the case of food products [20]. Water vapor and oxygen are two key permeants studied in packaging applications, since they transfer from the internal or external environment through the polymer package wall, causing a continuous change in product quality and often decreasing the intended shelf-life. Carbon dioxide is now important for the packaging in modified atmosphere packaging (MAP) technology because the issues with processed fresh product can be addressed, leading a significantly longer shelf-life [20].

To meet high demands for barrier properties of water vapor, oxygen, and grease ingress, the formation of a multilayer structure is often essential. Multilayered structures are well established in the packaging industry, with examples including biopolymer coatings with high oxygen barriers and fat resistance can be combined with a hydrophobic top coating to give the required water vapor barrier [43].

5.5 Antibacterial Properties

An active area in the research for new and developed materials for food packaging is the development of formulations with antimicrobial ability, where more than one substances with biocidal properties are included in a sachet, coated, adsorbed onto the materials surface or directly incorporated to the polymer during processing [219]. Various antimicrobials have been incorporated to polymer matrices for food packaging applications, such as organic acids [220], enzymes [221], bacteriocins [222], fungicides or other preservatives [132, 223].

Certain metal ions, such as copper, silver, zinc, palladium, or titanium, occur naturally and often essential minerals. These ions do not have adverse effects on eukaryotic cells below certain concentrations and can be ideal candidates for the implementation of novel safety measures [224].

Hence, metallic-based micro and nanocomposites (Table *9*) are being investigated and exploited in numerous food packaging applications. Recently, antimicrobial silver has emerged as a new cost-effective additive to prevent microbial proliferation on food contact surfaces. Although much of the research on silver compounds is still focused on medical applications [225], silver is currently incorporated to a wide variety of materials used in daily life, ranging from textile clothing [226], coatings in washing machines, refrigerators, furniture handles [227], to products where silver can be absorbed or ingested, such as water treatment units and food-contact materials [228].

Table 9. Antimicrobial metallic-based micro and nanocomposites in food packing [224]

Metal	**Size**	**Carrier**	**Microorganism**	**Log reduction**	**Food items**
Ag Zeolites	Micro	Stainless steel	Bacillus spp.	3 log10 CFU/mL	-
Ag Zeolites	Micro	Stainless steel	E. coli; P. aeruginosa; S. aureus	>6 log10 CFU/mL	-
AgNPs clusters	90 nm	PE	Alicyclobacillus acidoterrestris	2 log10 CFU/mL	Apple juice
Ag-clays, AgNPsAg-zeolite	NanoMicro	Chitosan	E. coli; Listeria; S. aureus; Salmonella	Inhibition zones	-
AgNPs	15–25 nm	Polyvinylpyrrolidone	Psychrotrophic	10 days shelf-life increase	Asparagus spears
AgNPs	5–35 nm	Cellulose	K. pneumoniae	>5 log10 CFU/mL	-
AgNPs	5–35 nm	Cellulose	E. coli; S. aureus; Mesophilic	1–3 log10 CFU/mL	Meat, melon cuts
Ag-montmorillonite	Nano	Zein, agar, poly (ε-caprolactone)	Pseudomonas spp.	>2 log10 CFU/mL	-
CuNPs	20–60 nm	Cellulose	E. coli	Inhibition zones	-
CuNPs	10 nm	Chitosan	S. aureus; Salmonella	3–4 log10 CFU/mL	-
ZnO	200–400 nm	PVC	E. coli; S. aureus; Psychrotrophic	Inhibition zones, low decay	Apple cuts
Cu or ZnO	Nano	Hydroxyapatite	E. coli; S. aureus; C. albicans	1–2 log10 CFU/mL	-
TiO2	Nanophase	Stainless steel	E. coli	Inhibition zones	Meat exudates
TiO2	20 nm	EVOH	Bacillus spp.; E. coli; L. plantarum etc.	Self-sterility	-
TiO2	20 nm	Stainless steel	Biofilms of Listeria	3 log10 CFU/mL	-
TiO2	0.7–0.9 µm	Glass	E. coli; Listeria; S. aureus; Salmonella	2.8 log10 CFU/mL	Lettuce
TiO2	7 nm, 5 µm	Oriented PP	E. coli	1 log10 CFU/mL	Lettuce
ZnO, nisin	Nano	PLA on Glass	Salmonella enterica	3–4 log10 CFU/mL	Liquid egg
AgNPs, TiO2, ZnO	Nano	LDPE	Mesophilic	Shelf-life stable 28 days	Orange juice

AgNPs, TiO2, kaolin	Nano	PE	-	Better quality preserved	Jujube
AgNPs, TiO2, kaolin + hot air	Nano	LDPE	P. citrinum; yeasts and moulds	Decay decrease	Bayberries

However, the problem arising from the use of metals in food contact surfaces depends on the quantity of ions able to migrate into the food matrix [224]. Some articles, such as plastics, recycled plastics, active and intelligent materials fall within specific regulations. Commission Regulation (EC) No 4502/2009 [229] related to active and intelligent packaging points out that the active element necessitates identification and active materials require information on permitted uses, and maximum quantity released by the active component. Concerning the use of nanoparticles, the corresponding legislation is not yet fully developed.

Among other polymers, chitosan has received a significant attention as antimicrobial film-forming agent for food preservation to the researchers due to its biodegradability, biocompatibility, cytotoxicity, and antimicrobial activity [230]. Chitosan is a linear polysaccharide consisting of (1,4)-linked 2-amino-deoxy-β-d-glucan, is a deacetylated derivative of chitin, which is the second most abundant polysaccharide found in nature after cellulose [230]. As compared with other bio-based food packaging materials, chitosan has the advantage of being able to incorporate functional substances such as minerals or vitamins and possesses antibacterial activity [231]. A number of studies on the antimicrobial characteristics of films made from chitosan have been carried out earlier [232, 233].

5.6 Biodegradation behavior

Degradation is an irreversible change in the chemical structure of polymers that causes a deleterious change in their properties [234]. Typically polymers can be degraded by mechanisms such as photodegradation (UV light), oxidation by chemical additives, thermal degradation by heat, mechanical degradation by various mechanical effects and biodegradation by microorganisms [235]. According to International Standardization Organization (ISO) and European Committee for Standardization (CEN) [236], biodegradation is the degradation caused by biological activity, especially by enzymatic action, leading to significant changes in the chemical structure of the exposed material and resulting in the production of carbon dioxide, water, mineral salts (mineralization) and new microbial cellular constituents (biomass) [237]. Biodegradation can occur under two different conditions: aerobic in the presence of oxygen and anaerobic with no oxygen available [234]. Several international organizations legislate standards for testing biodegradability of polymeric materials. A list of the most commonly used tests is provided in *Table 10*.

Table 10 A List of Standard Tests for Biodegradability of Food Packaging [144]

Standard	Environment
ASTM D6400	Standard specifications for compostable plastics
ASTM 5338-98 (2003) = ISO 14852	Controlled compost
ASTM D5988-03 = ISO 17556:2003	Aerobic biodegradation in soil
ISO CD 14855	Compost
ASTM D5209-91	Aerobic, sewer sludge
ASTM D5210-92	Anaerobic, sewer sludge
ASTM D5511-94	High-solids anaerobic digestion
ISO 14855	Aerobic biodegradation under controlled conditions
ISO 14852	Aerobic biodegradation in aqueous environments
ISO 15985	Anaerobic biodegradation in a high-solids sewerage environment
CEN 13432; ISO 14855; ISO 14855 (respirometric); ISO 14852; ASTM D5511-94; ASTM D5152-92; ASTM E1440-91; modified OECD 207; CEN TC 261/SC4/WG2	European standard for biodegradability for polymers and packaging; incorporates other standards and tests

Biocomposites with natural fillers have become a major part of the biodegradable plastics industry, because natural resource fillers are abundant, inexpensive, renewable, and fully biodegradable raw materials [24]. Biodegradability of biocomposites were studied and investigated by many researchers where usually weight loss over time was considered as a result of biodegradation.

Biodegradation of biocomposites is faster for the composites with higher natural fiber/filler content [173, 204, 238, 239]. However, chemical treatment of fiber/filler or using grafted copolymer decelerate the biodegradation process in biocomposites. Biodegradability of PLA/corn starch biocomposites in Proteinase K solution (50 mM Tris-HCl buffer, pH 8.6) and soil (potting media, vermiculite, and composting microorganisms) at 30ºC and 80% relative humidity was investigated [240], where degradation using Proteinase K was faster than in soil. However, in both cases, biocomposites with coupling agent showed slower degradation than the ones without coupling agent. Thus, the improved interfacial adhesion due to the coupling agent impedes PLA degradation. The degradation of pure PLA was slower than its biocomposites. Similar results were observed by others [173, 204, 238, 239] as well. Acrylic acid grafted PLA/starch biocomposites was prepared and buried in soil (alluvial-type) [204], where starch degradation was claimed as the dominant reaction in the former stage, and PLA degradation in the latter stage (after six weeks).

Biodegradation of PLA is slower than other biodegradable aliphatic polyesters [239]. It was found that the order of higher weight loss after the burial was PCL>PHBV>PBS>PLA. The weight loss of PCL after 180 days was 45%, while no weight loss was observed for PLA in their study.

Industrial composting is the fastest method for biodegradation of biopolymer and their composites [241]. Industrial composting is the controlled biological decomposition of organic waste under managed conditions that are predominantly aerobic and that allow the development of thermophilic conditions as a result of biologically produced exothermic heat [242]. In the course of industrial composting operations, biomass is mixed more frequently and moisture and oxygen content and temperatures are higher (50–70 °C) than during domestic composting.

5.7 Life cycle and Environmental Impact

The design of materials should not only consider the choice of renewable resources as raw materials for their preparation, but also should be completely sustainable throughout their life cycle, including synthesis, usage, and waste management [243]. The design and manufacture of biocomposites should be performed using local natural resources, which will contribute to a sustainable regional development and a reduction in the transport costs and associated environmental impacts [244].

Eco-friendly biocomposites are defined as composite materials that combine lignocellulosic natural fibers including hemp, sisal, jute, and kenaf with biodegradable polymers [71] to offer sustainability benefits additionally [31]. The concept of sustainable bio-based products is shown in *Figure 17*, which states a bio-based product is derived from renewable resources with recycling capability and triggered biodegradability, i.e., stable in their intended lifetime but would biodegrade after disposal in composting conditions with commercial viability and environmental acceptability is defined as a sustainable bio-based product [245].

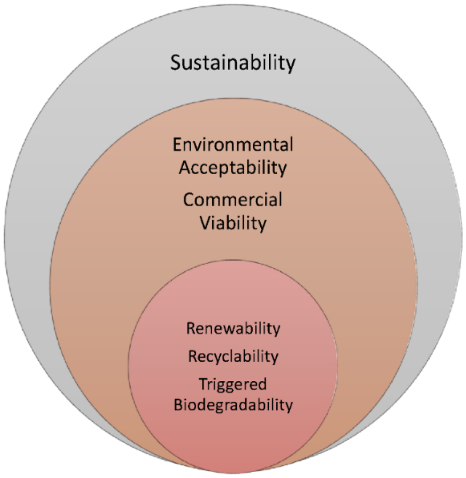

Figure 17. The concept of “sustainable” bio-based product.

Once manufactured, products made from sustainable biocomposites must satisfy the requirement that no harmful effects to the environment or to human health will be derived throughout their service life in the proposed application. If biocomposites are to be vended on their environmental credentials, it is important that these are validated by life cycle assessment (LCA) or other trustworthy means [91]. Using a cradle to grave approach, an LCA analysis considers all environmental impacts and calculates the mass and energy flows during manufacturing and end use. The direct and indirect environmental impacts determined quantitatively and correlated to the environmental impacts from all steps. The LCA framework is regulated by ISO 14040 to 14043 standards [246].

Polysaccharides are among the most important renewable resources for humankind. Although it cannot be stated with absolute certainty that polysaccharide-based products are better than their petrochemical-based counterparts from an environmental point of view, but important advantages do exist. A recent review [247] confirms that from cradle to grave, in terms of non-renewable energy requirements and greenhouse gas (GHG) emissions, the polysaccharide products are better than their conventional counterparts, which are mostly petrochemical-based materials.

A life cycle assessment on a thermoformed yogurt cup [248] revealed that PLA is a more energy efficient polymer than PP. This is because PLA consumes almost no feedstock energy. However, the difference between the two systems becomes marginalized when the uncertainty of the estimates is taken into consideration, since life cycle inventories are data intensive and data quality significantly influences results. PLA and PP greenhouse gas emissions are equivalent if carbon embodied in PLA is assumed to be fully sequestered in landfill. Uncertainties in PLA biodegradation in a landfill can bear a substantial impact on the estimates of greenhouse gas emissions.

Life cycle energy consumption and GHG emissions of PLA and PS trays [249] showed PLA trays generating lower GHG emissions than PS trays by 16.04%, but the energy consumption to produce PLA trays was slightly higher (4.06%) than that for PS trays, where PLA pellets production was hypothetically assumed to be derived from biomass feedstock locally [250]. However, different waste management scenarios result in variable end scenarios in cradle-to-grave assessment. The results suggested that composting or landfill with energy recovery from methane collection was suitable for PLA trays, while incineration with energy recovery also appropriate for PS trays. The LCA study on PLA and PET bottles for drinking water also could not find any superiority of PLA on the PET [251]. The environmental impact of bio-based food packaging can be reduced when suitable waste treatment is applied [252].

In LCA studies, obtaining the resin and supplies closest to the manufacturer and variation of the end-of-life scenario have massive impact in a majority of the cases [253]. Thus, the distance and type of transportation system used to distribute the packaging systems cause the design of the system to show a different environmental impact.

The dominating environmental issues in the food packaging area have been material use and recycling possibilities, and not the reduction of food losses [5]. However, new packaging solutions should not only reduce the environmental impact from the packaging itself, but also reduce food losses. [254]. The total environmental impact will increase if food losses increase, even if the impact from the packaging decreases [255]. Therefore, efficient packaging design is very important to reduce overall environmental impact and food losses.

The environmental superiority of biocomposites compared to conventional composites is still under examination because of their relatively excessive processing requirements, which in turn consumes more energy.

6 Future Directions & Conclusions

The development of biodegradable biocomposites and its related products is increasing. Non-food crops and other bio-renewable resources offer a virtually limitless supply of renewable and potentially sustainable raw materials for the production of biocomposites. In parallel, significant developments have been witnessed in the realm of biopolymers in recent years. Therefore, biocomposites are expected to see a period of sustained growth. However, investment is still necessary in research and development if a sustainable biocomposites industry is to be extensively established. Currently, the main markets for biocomposites are the construction and automotive sectors. With further developments and improvements in performance, new opportunities and applications such as packaging will accelerate.

Although biocomposites are receiving attention, the challenge remains in replacing conventional composites with comparable structural and functional stability during storage, use, and environmental degradation on disposal [68]. In addition, there is a need for product standards to support the performance of the products.

Despite the uncertainties and assorted assumptions, it can be concluded that biopolymers and natural fibers offer important environmental benefits today and for the future. Compared to conventional materials, the biocomposites can clearly contribute to the goals of saving energy resources and mitigating GHG emissions [256].

Key activities to reach the goal will be the identification of raw material extraction, sustainable crop growth, implementation of biocomposites interfacial properties, material processing and product manufacture, safe service life in the intended application, and product design [90]. Their individual properties should be a solid base to generate new applications and opportunities for biocomposites in the 21st century ‘‘green’’ materials environment.

Significantly, the antibacterial packaging should be safe to handle as well as do not release toxic elements into foods. Hence, experts from different disciplinary such as food technologists, microbiologists, chemists, polymer technologists, chemical engineers, as well as environmental scientists should work towards a remarkable application and commercialization of eco-friendly antibacterial packaging products. Such antibacterial biodegradable biocomposites are promising food packaging materials because its biodegradability provides sustainable development for future society.

Currently bio-based packaging materials are used in packaging for short shelf-life products, such as fresh fruits and vegetables, and long shelf-life products, such as pasta and chips, which do not require high oxygen and/or water barrier properties. However, the portfolio of biocomposites shows a wide variety in properties, which could make them also applicable as a packaging material for other food products, like modified atmosphere packaging (MAP). Testing and analysis should be carried out to ensure that these packaging could be used commercially.

Biopolymers satisfy the environmental concerns but they show some limitations in terms of performance like thermal resistance, barrier, and mechanical properties, associated with the costs. Research towards enhancing barrier properties, to incorporate intelligent labelling, to give to the consumer the possibility to have more detailed product information than the current system is required. The bioplastics require competing on the performance as an additional benefit, other than just being produced of biologically resources.

Nanotechnology shows numerous opportunities for improving biocomposite products by providing nanotechnology-based coatings to increase water uptake, reduce biodegradation and volatile organic compounds and even flame resistance. Regardless, the many benefits of bio-nanocomposite materials, the use of nanofillers to produce the materials need proper considerations in terms of safety for end use because there are limited studies performed on the toxicological effects and migration of nanofillers into food from the packaging films.

A more wide-ranging integrated approach, encompassing economic, social, and environmental considerations, together with more efficient, recyclable packaging designs, is the key to sustainable packaging. Only through the mindful combination of sustainable crop growth, raw material extraction, synthetic and modification steps, material processing and product manufacture, safe service life in the intended application, and suitable waste management will be able to achieve the true goal of sustainable development in material and product design.

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2.2 Paper-II: Antibacterial Properties of Hemp and Other Natural Fibre Plants: A Review

Khan, B. A, Warner, P and Wang, H. (2014). Antibacterial Properties of Hemp and Other Natural Fibre Plants: A Review. BioResources Vol. 9, Issue 2, pp 3642-3659)

Plants contain numerous biologically active compounds, many of them are antibacterial. Some natural fibre plants, such as hemp, are regarded to possess antibacterial activity against a wide range of pathogenic bacteria. This review aimed to compile the relevant investigations on antibacterial activity of hemp including other fibre plants. It provides a critical study featuring an insightful analysis of the potential application of antibacterial hemp in biocomposites.

Antibacterial Properties of Hemp and Other Natural Fibre Plants: A Review

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Intervention against pathogenic bacteria using natural plant material has a long history. Plant materials also have been widely used as fillers and/or reinforcers in polymer composites. Some natural fibre plants, such as hemp, are regarded to possess antibacterial activity against a wide range of pathogenic bacteria. Innovative applications can be explored if they are incorporated in polymer composites. This review aims to compile the relevant investigations on antibacterial activity of hemp and other fibre plants such as jute, flax, kenaf, sisal, and bamboo. The antibacterial character might be contributed from cannabinoids, alkaloids, other bioactive compounds, or phenolic compounds of lignin. This review is intended to encourage utilization of hemp and other natural fibre plants in value-added diversified products. Some potential applications are also discussed.

Keywords: Hemp; Natural fibre; Antibacterial activity; Cannabinoids; Composites

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INTRODUCTION

Plants are a great source of natural fibres that can be classified as primary fibre plants or secondary fibre plants, depending on their utilization. Cotton, jute, hemp, flax and kenaf are some examples of primary fibre plants that are grown for their high fibre content, while pineapple, oil palm, and coir are secondary fibre plants where the fibres are produced as a by-product (Faruk *et al.* 2012). Natural fibre plants have been used in textiles, composites, and many other sectors (Kalia *et al.* 2009).

The use of plants in medications has a long history, and it was usually the only method available in previous eras (Redo *et al.* 1989). Interest in plants having antibacterial properties has been revived for many reasons, such as the public becoming increasingly aware of problems with the over-prescription and misuse of synthetic antibiotics (Cowan 1999). Antibacterial activity of plant materials is applicable not only in medications but also in various commodities, for example packaging and cosmetics that are used in our everyday life. Antibacterial activity of natural fibre plants can generate more opportunities for innovations. Historically, after fibre extraction from primary fibre plants, the rest of the plant material has had very limited use. However, antibacterial investigations of natural fibre plants may provide improved utilization of these by-products as well.

Hemp is a typical fibre-generating plant with well-known antibacterial performance (Appendino *et al.* 2008; Lone and Lone 2012). Certain other natural fibre plants also show similar properties (Afrin *et al.* 2012; Farah *et al.* 2006; Ilhan *et al.* 2007; Santos *et al.* 2009; Zakaria *et al.* 2011). However, hemp is more highly regarded as a potential medicinal plant and has received more attention than other fibre plants (Benet 1975).

To more fully understand the implications of research that has been done on the antibacterial properties, this review includes different aspects such as the identities and concentrations of active components, the antibacterial activity of extracts, and possible applications. Such observations can provide a basis for the future inclusion of natural fibre plants in composites as antibacterial agents. The main objective of this review is to encourage utilization of hemp and other natural fibre plants in value-added diversified products based on their antibacterial performance.

BACTERIA AND ANTIBACTERIAL METHODS

Before beginning a discussion on the antibacterial activity of natural fibre plants, it would be useful to give some introductory information on pathogenic bacteria and the intervention methods currently being practiced. Pathogens can be defined as those microorganisms that may cause illness in humans, transmitted via air, water, food, or other vectors. A wide range of enteric pathogens and their toxins that can be transmitted via food include the bacteria (such as *Campylobacter* species, *Salmonella* spp., *Shigella* spp., *Escherichia coli, Clostridium botulinum, Listeria monocytogenes, Clostridium perfringens, Bacillus* spp., *Staphylococcus aureus, Cryptospordium parvum, Cyclospora cyatenenesis*, and *Giardia* spp.) and viruses (such as Norwalk-like viruses and Hepatitis A) (Commission 2002). Of the four pathogen types (*i.e.*, bacteria, fungi, parasites, and viruses), it was found that over 90 percent of confirmed foodborne human illness cases and deaths reported to the Centers for Disease Control and Prevention (CDC) are attributable to bacteria (Bean and Griffin 1990; Bean *et al.* 1990).

Various intervention methods are in use to control bacteria. Inactivation of bacteria can be achieved by chemical and/or physical means, such as heat, chemical solutions, gases, and radiation (Curtis 2008; Laroussi and Leipold 2004; Parish *et al.* 2003). Preservative agents are used to ensure that foods remain safe and unspoiled. Weak organic acids, hydrogen peroxide, and chelators are the examples of chemical preservative agents. Naturally occurring preservatives such as small organic antimicrobial biomolecules (for example, benzoic acid, vanillic acid, benzaldehyde, ferulic acid, estragole, guaiacol, and eugenol), antimicrobial proteins and peptides, and cell wall perturbing biomolecules are used as well (Brul and Coote 1999).

ANTIBACTERIAL PROPERTY OF NATURAL FIBRE PLANTS

Plants contain numerous biologically active compounds, many of which have been shown to have antibacterial properties (Cowan 1999; Redo *et al.* 1989). Researchers from divergent fields in the world have investigated plants with an eye to their antibacterial usefulness. Useful antimicrobial phytochemicals identified in the plants can be divided into several categories such as phenolics and polyphenols, terpenoids and essential oils, cannabinoids, alkaloids, lectins and polypeptides, and polyacetylenes. Phenolics and polyphenols include simple phenols and phenolic acids, quinones, flavones, flavonoids, flavonols, tannins, and coumarins (Appendino *et al.* 2008; Cowan 1999; Lone and Lone 2012). Much of the information about the antibacterial activities of plants is anecdotal, although some of them have been scientifically investigated. The antimicrobial properties of the constituents from a wide variety of plants have been reviewed (Cowan 1999; Dixon 2001; Dorman and Deans 2000). Some of the fibre plants, especially hemp, demonstrated potentially important antibacterial properties.

Hemp

Hemp has a long history of cultivation for various purposes including fibre, medicine, recreational drugs, and food (Marks *et al.* 2009). Hemp varieties can be divided into fibre type, intermediate type, and drug type (known as marijuana) with the Δ^9-trans-tetrahydrocannabinol (Δ^9-THC) content ranging from <0.3%, 0.3 to 1.0%, and 1 to 20%, respectively (Ahmed *et al.* 2008; Grotenhermen and Russo 2002).

Bioactive constituents

Hemp contains many classes of chemical constituents (Turner *et al.* 1980), with compounds constantly being discovered and reported. These include cannabinoids, nitrogenous compounds, amino acids, proteins, glycoproteins, enzymes, sugars, hydrocarbons, simple alcohols, simple aldehydes, simple ketones, simple acids, fatty acids, simple esters, lactones, steroids, terpenes, non-cannabinoid phenols, flavanoid glycosides, vitamins, and pigments. The total number of natural compounds identified in hemp is greater than 500 (ElSohly and Slade 2005; Radwan *et al.* 2008). Complex macro-composition of hemp and numerous compounds within the plant have the potential to exhibit antibacterial activity.

Cannabinoids are the typical group of C21 compounds present in hemp, and they are in the form of carboxylic acids, analogs, and transformation products (Mechoulam and Gaoni 1967; Razdan 1986). The compounds are either structurally or pharmacologically similar to Δ^9-THC or those that bind to the cannabinoid receptors. The 86 known cannabinoids (Ahmed *et al.* 2008; ElSohly and Slade 2005; Radwan *et al.* 2008a,b) from hemp plant can be classified into 11 structural types: cannabigerol (CBG), cannabichromene (CBC), cannabidiol (CBD), Δ^9-THC, Δ^8-THC, cannabicyclol (CBL), cannabielsoin (CBE), cannabinol (CBN), cannabinodiol (CBND), cannabitriol (CBT), and miscellaneous types. In hemp, the most prevalent cannabinoids are Δ^9-THC, CBD, and CBN, followed by CBG, CBC, and CBND. The others are minor. Some cannabinoids extracted from hemp were found to show excellent antibacterial activity (Appendino *et al.* 2008; Lone and Lone 2012; Radwan *et al.* 2009).

There are three sources of cannabinoids. Plant-derived cannabinoids sometimes termed phytocannabinoids (Lambert and Fowler 2005) such as Δ^9-THC and CBD, occur uniquely in the hemp plant. Endogenous cannabinoids, also known as endocannabinoids (such as anandamide and 2-arachidonoylglycerol), are produced in the bodies of humans and animals. Synthetic cannabinoids, such as WIN-55, 212-2, JWH-133, and (R)-methanandamide (MET), have been developed in the laboratory with structures similar to plant or endogenous cannabinoids (Sarfaraz *et al.* 2008).

Active components in different parts of hemp

The concentrations of bioactive compounds in hemp depend on tissue type, age, variety, growth conditions (nutrition, humidity and light levels), harvest time, and storage conditions (Hirofumi *et al.* 1980; Keller *et al.* 2001; Ross and El Sohly 1996). For example, the hemp grown in northern latitudes is reported to have a high content of CBD and Δ^9-THC, resulting in strong antimicrobial activity (Leizer *et al.* 2000). Cannabinoids are found in all parts of the hemp plant, but the most potent resinous exudate comes from the flowering tops. The potency of the clinical effects of cannabinoids is determined by the type of seed and the part of the plant being used but not by the climate or soil, as had once been assumed (Walsh *et al.* 2003). Fairbairn and Liebmann (1974) reported that a cool climate and poor lighting conditions do not seem to prevent the production of active components *i.e.* THC and CBD. It has been found that the concentration of THC varies between and within individual plants (Fairbairn and Liebmann 1974; Latta and Eaton 1975). Seasonal fluctuation in cannabinoids has been related to stage of development of the plant (Latta and Eaton 1975). Cannabinoids were lowest in seedlings, highest prior to flowering, and at an intermediate level thereafter until physiological maturity. It was also noticed that cannabinoids were highest in flowers and progressively lower in leaves, petioles, stems, seeds, and roots; however, cannabinoids content of male and female flowers was not significantly different (Latta and Eaton 1975). Most of the investigations on cannabis concentration of hemp plants excludes the roots, stems, and seeds as their cannabinoid content are low (Field and Arndt 1980). Table 1 shows the concentration of bioactive components in hemp in descending order by different parts and by the growing stage of the plant.

Table 1. Concentration of Active Components within the Plant

Different parts of the plant	Growing stage
Flowers	Prior to flowering
Youngest leaves of uppermost nodes	From flowering to physiological maturity
Older leaves along the axis	Seedlings
Petioles	
Stems/hurd	
Outside of the Seeds	
Seed coat and kernel	
Roots	

Hemphill *et al.* (1980) reported that cannabinoid content varied quantitatively and qualitatively in different organs of hemp plants of different geographical origins. Leaves of different ages were analysed, and it was revealed that the youngest leaves from the uppermost nodes of the flowering plants of fibre type strains contained the highest level of their characteristic cannabinoid. The concentrations of cannabinoids in fibre type hemp plants decreases progressively along the axis, with the lowest level of cannabinoids present in the mature and old senescing leaves. Again, bracts of fibre type plants possess high level of CBD and low level of Δ^9-THC, while bracts from the drug type plants contained high levels of Δ^9-THC with low concentrations of CBD or CBC.

Analysis of hemp seeds of both drug type and fibre type for their Δ^9-THC concentration has been carried out by Ross *et al.* (2000). It was noticed that cleanliness of the seeds plays a major role in the apparent concentration of Δ^9-THC in hemp seeds. Investigation also suggested that the bulk of Δ^9-THC in the hemp seeds resides on the outside of the seeds, with only small amounts in the seed coat or the kernel itself (Ross *et al.* 2000). Thus the content of THC in hemp oil can come only as a result of the technical process of harvesting the fruits (Mölleken and Husmann 1997).

Antibacterial performance

Extraction, which separates bioactive compounds of the plant tissues from the inactive/inert components, is the most frequently used method to evaluate antibacterial effect of plant materials. Common solvents used for active component extraction are water, ethanol, methanol, chloroform, dichloromethanol, ether, and acetone (Cowan 1999; Ncube *et al.* 2008). Solvents used in the extraction methods have great influence on the amount of active compounds that can be extracted and thus the result of the antibacterial performance of a plant.

Hemp extracts using organic solvents exhibited very good antimicrobial activity against *S. aureus*, as reported by Borchardt *et al.* (2008). Cannabinoids extracted from the hemp leaves by aqueous produced a total yield of 3.8 g, while an acetone extract produced a total of 4.8 g (Lone and Lone 2012). *In vitro* antimicrobial studies were conducted with aqueous, ethanolic, and petroleum ether extracts of the hemp leaves (Wasim *et al.* 1995). The acidic fraction was obtained from the ethanolic extract and 2% sodium hydroxide extract. The ethanolic extract, petroleum ether extract, and the acidic fraction exhibited activity both against Gram-positive and Gram-negative bacteria and also against the fungi used in the study. However, the aqueous extract did not show any antimicrobial activity.

Apart from the extraction method, several other factors also influence the results of antibacterial investigations, such as the environmental and climatic conditions under which the plant grew, choice of plant extracts, antibacterial test method, and the test microorganisms used (Nostro *et al.* 2000).

Researchers have reported antibacterial activity of cannabinoids against a wide range of bacteria (Appendino *et al.* 2008; Lone and Lone 2012; Radwan *et al.* 2009). Appendino *et al.* (2008) extracted all five major cannabinoids from hemp: CBD, CBC, CBG, Δ^9-THC, and CBN, and observed their antibacterial activity. It was found that all of them showed potent activity against a variety of *methicillin-resistant Staphylococcus aureus (MRSA)* strains of current clinical relevance. Lone and Lone (2012) extracted cannabinoids by aqueous and acetone and tested their antibacterial performance. The acetone extract exhibited higher antimicrobial activity than that of the crude aqueous extract against the bacteria *Pseudomonas aeruginosa* and *Vibro cholera,* and the fungi *Cryptococcus neoformans* and *Candida albicans*.

The cannabinoids extracts also demonstrated antioxidant activity by changing to yellow colour. Radwan *et al.* (2009) isolated nine new cannabinoids from a high-potency variety of hemp. Three of these displayed significant antibacterial and antifungal activities, while others displayed strong antileishmanial activity. Crude alkaloid from the leaves of hemp plants was extracted, and its *in vitro* antibacterial activities were evaluated against various bacterial strains of microflora and a β-strain of *E. coli* (Das 2012). The study revealed growth inhibition and effectiveness in the extracts of hemp, which suggests that leaves potentially possess a broad spectrum antibacterial activity. Considering the above findings, it is certain that all five major cannabinoids: CBD, CBC, CBG, Δ^9-THC, and CBN, and crude alkaloids from hemp are potential candidates to be considered as natural antibacterial agents. Table 2 summarizes antibacterial activity found in hemp extracts.

Table 2. Antibacterial Activity of Hemp Extracts

Extracts	Activity	Reference
Five major cannabinoids (CBD, CBC, CBG, Δ9-THC, and CBN)	Potent activity against a variety of methicillin-resistant *S. aureus* (MRSA) strains	Appendino *et al.*(2008)
Cannabinoids (crude aqueous acetone extract of leaves)	Inhibition against bacteria *P. aeruginosa*, *V. cholerae* and fungi *C. neoformans*, *C. albicans*.	Lone and Lone (2012)
(±)-3''-hydroxy-$\Delta^{(4'',5'')}$-CBC, 4-acetoxy-2-geranyl-5-hydroxy-3-n-pentylphenol and 8-hydroxycannabinolic acid	Good anti-*S. aureus* activity, antifungal activity against *C. albicans*	Radwan *et al.* (2009)
Crude alkaloid	Mouth, skin, ear microflora and *β-strain of E. coli*	Das (2012)
Seed oil	Pronounced activity against *B. subtilis* and *S. aureus*, moderate activity against *E. coli* and high activity against *P. aeruginosa*	Ali *et al.* (2012)
	Inhibit the growth of *A. niger*, *E. coli*, *S. aureus*, *S. cerevisiae*, and *P. aeruginosa*	Leizer *et al.* (2000)
Petroleum ether and Methanol extract of the whole plant	Pronounced antibacterial activity against *B. subtilis* and *S. aureus*, high activity against *E. coli*	Ali *et al.* (2012)
Ethanolic and Petroleum ether extracts of leaves	Exhibited activity against *B. subtilis, B. pumilus, S. aureus, M. flavus, P. vulgaris, B. bronchiseptica*	Wasim *et al.* (1995)
Aqueous-ethanol extracts of stems and leaves	Very good antimicrobial activity against *S. aureus*	Borchardt *et al.* (2008)
Essential oil	Excellent activity against *C. sporogens, E. faecium, S. salivarius* subsp. *thermophiles, P. carotovorum* subsp. *carotovorum, P. savastanoi pv. phaseolicola*	Nissen *et al.* (2010)
	Modest activity against *A. hydrophyla, B. subtilis, B. natriegens, B. linens, B. thermosphacta, E. coli, F. suaveolens, M. luteus, S. aureus and Y. enterocolitica*	Novak *et al.* (2001)

The antibacterial activity of hemp seed oil, essential oil, and organic solvent extracts has been studied (Ali *et al.* 2012; Borchardt *et al.* 2008; Leizer *et al.* 2000; Nissen *et al.* 2010; Novak *et al.* 2001; Wasim *et al.* 1995). Ali *et al.* (2012) investigated seed oil, and petroleum ether, and methanol extracts of the whole hemp plant for their antimicrobial activity against two Gram positive organisms (*B. subtilis* and *S. aureus*), two Gram negative organisms (*E. coli* and *P. aeruginosa*), and two fungi (*Aspergillus niger* and *C. albicans*) using the cup plate agar diffusion method. They found that the seed oil produced pronounced antibacterial activity of inhibition against *B. subtilis* and *S. aureus*, moderate activity against *E. coli*, and high activity against *P. aeruginosa*. They were inactive against the two fungi tested. The petroleum ether extract of the whole plant exhibited pronounced antibacterial activity against both *B. subtilis* and *S. aureus* organisms, high activity against *E. coli*, and was inactive against *P. aeruginosa* and both fungi. The methanol extract of the whole plant also showed pronounced antibacterial activity against *B. subtilis*, low activity against *S. aureus*, and high activity against both Gram negative organisms, while being inactive against *A. niger* and having low activity against *C. albicans*.

Another study examined the inhibitory activity of freshly extracted essential oils from three fibre type hemp varieties (Carmagnola, Fibranova, and Futura) on microbial growth (Nissen *et al.* 2010). The results showed that essential oils of industrial hemp can significantly inhibit the microbial growth, depending on variety and sowing time. Novak *et al.* (2001) found that the essential oils of five different cultivars of hemp had modest antibacterial property.

Linking an antibacterial functional group with the cellulosic backbone of hemp fibre may offer opportunities to produce functionalized biopolymer for biomedical applications. Cassano *et al.* (2013) prepared material via esterification of hemp with 2-benzyl-4-chlorophenol, a germicidal agent, which was covalently coupled to cellulose backbone of hydrophilic fibers by a heterogeneous synthesis, to produce a functionalized biopolymer with a satisfactory degree of substitution. Its antibacterial activity in inhibiting *S. aureus* and *P. aeruginosa* growth in Petri dishes suggested that this biomaterial possesses an excellent *in vitro* antibacterial activity and so it can be efficiently employed in biomedical fields to ensure a protection against contaminations. The functionalized biopolymer interacts with metal ions because of its chelating functional groups. This feature makes the synthesized biomaterial a potential candidate for metal ions removal.

Negative results regarding antibacterial activity of hemp also have been reported (Sokmen *et al.* 1999; Yasmeen *et al.* 2012). Air-dried and finely ground samples of hemp seeds were extracted in methanol at 60 °C for 6 h, and the extract was tested against *S. aureus*, *B. cereus*, *B. catarrhalis*, *E. coli*, *C. perfringens* and *C. albicans*. The extract did not exhibit any activity against any of the microorganisms (Sokmen *et al.* 1999). Aqueous and alcoholic extracts of hemp were evaluated for their *in vitro* antibacterial activity against *P. mirabilis* by serial dilution methods (Yasmeen *et al.* 2012). Both the aqueous and alcoholic extracts of hemp did not show any antibacterial activity against *P. mirabilis*.

In general, cannabinoids, alkanoids, seed oil, essential oils, methanol extracts, ethanolic extracts, acetone extracts, and petroleum ether extracts of whole hemp plant or leaves showed antibacterial effect against a variety of bacteria. Hemp may have many applications in controlling microorganism; however, no products have been reported.

Antibacterial activity of hemp hurd

Lignin, the second most abundant natural compound after cellulose (Boudet and Grima-Pettenati 1996), is a high-molecular weight polymer of phenolic compounds that occurs naturally in plants. The phenolic components of lignin have been reported to inhibit growth of micro-organisms such as *E. coli, S. cerevisiae, B. licheniformis*, and *A. niger* (Baurhoo *et al.* 2008; Zemek *et al.* 1979). Some studies discovered that lignin in bamboo (Afrin *et al.* 2012), lignin in corn stover (Dong *et al.* 2011), as well as lignin in cotton stalks and bagasse (Nada *et al.* 1989) demonstrated potent antibacterial activity. The total amount of lignin in bamboo may vary between 26.8% to 30.1% of the weight (Sekyere 1994). Afrin *et al.* (2012) claimed that antibacterial agents of bamboo (*Phyllostachys pubescens*) are located in lignin (aromatic and phenolic functional groups in lignin). Phenolic acids and aldehydes identified from alkaline nitrobenzene oxidation of bamboo are vanillin, syringic acid, syringaldehyde, vanillic acid, p-hydroxybenzaldehyde, p-hydroxybenzoic acid, p-coumaric acid, acetosyringone, acetovanillone, and ferulic acid (Li *et al.* 2010).

Hemp hurds have high content of lignin (19 to 21%) and hemicellulose (31 to 37%), but lower amount of cellulose (36 to 41%) (Thygesen *et al.* 2007). Phenolic acids and aldehydes identified in hemp hurd are vanillin, syringaldehyde, p-hydroxybenzaldehyde, vanillic acid, syringic acid, p-coumaric acid, acetosyringone, and gallic acid (Gandolfi *et al.* 2013). It is clearly evident that the phenolic compounds identified in hemp lignin are similar to those in bamboo. Besides, cannabinoid content of fibre type hemp hurds was investigated by Cappelletto *et al.* (2001). The cannabinoid (Δ^9-THC, CBD, Δ8-THC, and CBN) content of the dust obtained from the top of the stems after the mechanical treatment can be up to 1.3% of dry matter. Considerable amount of cannabinoids present in hemp hurd as well as the phenolic compounds that hemp hurd might possess good antibacterial property.

Other Natural Fibre Plants

Among all the fibre producing plants, hemp has been the most predominantly investigated plant for bioactive components. Other fibre plants such as jute, bamboo, flax, sisal, kenaf, banana, and pineapple, have also been investigated and have shown some antibacterial activity.

Bamboo

Bamboo belongs to the family of Poaceae (grasses), sub-family (Bambusoideae) and tribe (Bambuseae) (Worobiec and Worobiec 2005). The main constituents of bamboo culms are cellulose, hemicellulose, and lignin, which account for over 90% of the total mass. It also contains about 2 to 6% starch, 2% deoxidized saccharide, 2 to 4% fat, and 0.8 to 6% protein. Alpha-cellulose, lignin, extractives, pentosan, ash, and silica content are increased with increasing age of bamboo (Chen *et al.* 1985; Yusoff *et al.* 1994).

It is well accepted that there are abundant biologically active components in bamboo, such as triterpenoids, saponins, and sterols (Chen *et al.* 2002). Several phenolic compounds have been identified in the culms and leaves. Composition and concentrations of soluble phenolic compounds (phenolic acids and flavonoids) in bamboo culms are affected by species, age and site (Keski-Saari *et al.* 2008).

Antibacterial performance of bamboo extracts was reported, where methanol, ethanol, and other common solvent extracts of bamboo culms, shavings, and leaves were tested against a wide variety of bacteria (Mulyono *et al.* 2013). Afrin *et al.* (2012) claimed that antibacterial agents of bamboo (*Phyllostachys pubescens*) are located in lignin, not in hemicellulose or other water-soluble chemical components. In this case, extraction was done with raw bamboo powder in water, dimethyl sulphoxide (DMSO), and aqueous dioxane, since DMSO and dioxane are regarded as commonly used solvents for hemicellulose and lignin respectively.

Jute

Jute fibre is obtained from two cultivated species *Corchorus capsularis* and *C. olitorius*. Cardiac glycosides, triterpenoids, sterols, phenolics, ionones, carbohydrates, and fatty acids have been reported from jute (Khan *et al.* 2006; Kohda *et al.* 1994). Mosihuzzaman *et al.* (1982) identified low molecular weight carbohydrates, inositols, lignin, glycosidic, and ester-linked phenolic acids in the bark, stick, and fibre of the jute plant. Analysis of lignin and cinnamic acids in jute using analytical pyrolysis and Fourier-transform infrared (FTIR) spectroscopy was carried out, and around 80 compound were identified (del Rio *et al.* 2007).

The antibacterial activities of the petroleum ether, methanol and ethyl acetate+water extracts from the jute plant sample were evaluated. The petroleum ether extract of jute leaves demonstrated activity against *E. coli, S. aureus*, and *Y. enterocolitica*. The ethyl acetate+water extract was effective against *G. candidum* and *B. cinerea* (Ilhan *et al.* 2007). Antibacterial activity of the jute plant also has been reported by other researchers (Adegoke and Adebayo-Tayo 2009; Patel Rashmika 2011). Farah *et al.* (2006) demonstrated the potential use of jute as an antibacterial agent against infections of *C. diphtheria*, *S. aureus, B. cereus*, *S. epidermidis*, and *K. rhizophila.*

Flax, Sisal, Kenaf, and others

Flax (*Linum usitatissimum*) belongs to the Linaceae family. Flax-seed contains many bioactive compounds, such as alpha-linolenic acid, lignans, and protein (Rubilar *et al.* 2010). Linseed oil or flax-seed oil showed good *in vitro* antibacterial activity against a number of microorganisms including *S. aureus*, *S. agalactiae*, *E. faecalis*, *C. albicans*, and *E coli* (Kaithwas *et al.* 2011). Antibacterial and antifungal activity of flax seed also has been reported by others (Guilloux *et al.* 2009; Rubilar *et al.* 2010; Xu *et al.* 2008).

Sisal belongs to the Agavaceae family. Fibres are obtained from leaves that are composed of 78% cellulose, 8% lignin, 10% hemicelluloses, 2% waxes, and about 1% ash by weight (Barkakaty 1976). Antibacterial activity of sisal plant was also reported in some literature (Dlamini Abednego *et al.* 2010; Santos et al. 2009). The hydroalcoholic extract obtained from sisal showed significant inhibition of *C. albicans* (Santos *et al.* 2009).

The kenaf plant (*Hibiscus cannabinus*) is composed of multiple useful components (*e.g.* stalks, leaves, and seeds) (Webber III and Bledsoe 2002). Antibacterial activity of Kenaf against *S. aureus* and *E. coli* was reported (Zakaria *et al.* 2011).

While cultivated primarily for their fruits, banana, and pineapple plants are also valuable source of plant fibre. Ethyl acetate, ethanol, and water soluble fractions of green banana peels, pulps, seeds, and inflorescences displayed high antibacterial and antioxidant activity (Fagbemi *et al.* 2009; Jain *et al.* 2011; Khan *et al.* 2010; Mokbe and Hashinaga, 2005; Padam *et al.* 2012). Pineapple stem waste exhibited antibacterial activity to some extent (Upadhyay *et al.* 2012).

POTENTIAL APPLICATIONS OF ANTIBACTERIAL HEMP

Contamination by microorganisms is of great concern in a variety of areas, such as medical devices, healthcare products, water purification systems, hospitals, dental office equipment, food packaging, food storage, and household sanitation (Patel *et al.* 2003). One possible way to manage microbial contamination is to develop materials with antimicrobial properties (Park *et al.* 2001). Application of hemp as drug and antibacterial agents have been reported (Moore *et al.* 2007).

Biomedical Applications

Biomedical application of polymer composites can be found in the form of implants and medical devices (Ramakrishna *et al.* 2001). In some applications the antibacterial property may increase the functionality of polymer composites, for example in wound dressing. These skin dressings should prevent loss of fluids, electrolytes, and other biomolecules from the wound and obstruct bacterial entry, but should also be permeable enough to allow the passage of discharges from pores or cuts. Hemp can be used in conjunction with suitable materials to meet these requirements. For example, polyurethane (PU) and chitosan are frequently used in wound dressings due to their excellent barrier properties and oxygen permeability (Khil *et al.* 2003; Mi *et al.* 2003). Hemp incorporated nanofibrous PU membrane, prepared by electrospinning, could be properly employed as wound dressings. Again, hemp incorporated asymmetric chitosan membrane may be a very useful wound dressing with the antibacterial capacity to prevent infection of broken skin. As well as the antibacterial property of hemp, its porous physical structure, air permeabilty, and absorbency capabilities would add advantageous features to wound dressing.

The lightweight, corrosion resistance, fatigue resistance, aesthetics, and ease of fabrication of polymer composite materials make them an ideal choice for modern limb systems (Ramakrishna *et al.* 2001). A large number of polymers such as polyethylene (PE), polyurethane (PU), polytetrafluoroethylene (PTFE), polyacetal (PA), polymethylmethacrylate (PMMA), polyethylene terepthalate (PET), silicone rubber (SR), polysulfone (PS), polyetheretherketone (PEEK), poly(lactic acid) (PLA), poly(glycolic acid) (PGA), and so on are used in various biomedical applications (Ramakrishna *et al.* 2001). Incorporating antibacterial hemp as filler in the polymer composites could provide protection against bacterial attachment. Hemp incorporated polymer composites can be an excellent choice for prostheses for external missing limbs such as legs and arms. Also, cannabinoids and alkaloids have the potential to be used as a drug to treat bacterial infection or may be used in conjunction with antibiotics to enhance their activity.

Food Packaging

In recent years, new food-packaging systems have been developed in response to trends in consumer preferences towards mildly preserved, fresh, tasty, and convenient food products with a prolonged shelf-life (Emamifar 2011). In addition, food-borne microbial outbreaks are driving a search for innovative ways to inhibit microbial growth in the foods while maintaining quality, freshness, and safety (Paola 2002). To provide this shelf-life extension, and to improve the quality, safety, and integrity of the packaged food, innovative active and intelligent packaging concepts are being developed. Examples of this are incorporating oxygen, moisture, and ethylene scavengers for oxygen, moisture, and ethylene sensitive foods, use of carbon dioxide or ethylene emitters in other foods, flavor imparting or scavenging chemicals, and antimicrobial agents for microbiological safety of food (Chinnan 2004). The application of antimicrobial agents to packaging can create an environment inside the package that may delay or even prevent the growth of microorganisms on the product surface and, hence, lead to an extension of the shelf life and/or the improved safety of the product. Antimicrobial packaging is a form of active packaging that interacts with the product or the headspace between the package and the food system, to obtain a desired outcome (Paola 2002). Although most of the antibacterial agents currently being used are usually artificial chemicals, natural plant material has the potential to be used in active packaging. For example, edible films incorporated with clove essential oil showed significant antibacterial activity against *L. acidophilus, P. fluorescens, L. innocua,* and *E. coli* (Gómez-Estaca *et al.* 2009). Similarly, hemp can be incorporated in food packaging composites, and be considered as ecofriendly. Hemp incorporated polymer composites formed by injection moulding can provide packaging materials with a wide range of shape and sizes for containing a range of foods including meat, salads, and ready-made food products. Essential oils of fibre type hemp may also have interesting applications in controlling spoilage by food-borne pathogens and phytopathogenic microorganisms.

Cosmetics

Hemp can be used for skin care and cosmetic due to the high content of oil, especially unsaturated fatty acids (Vogl *et al.* 2004). Antibacterial hemp in powder form can be incorporated into tooth powder, toothpaste, mouth-wash, toilet bars, antiseptic ointment, and foot powders. In hot weather, for example sweating and exercise generate a moisture-rich environment in shoes that stimulates overgrowth of both aerobic bacteria and fungi (Misner 2007). Antibacterial foot soakings may provide relief. Essential oil of hemp can also provide benefits in various cosmetics. An exposure and uptake assessment for Δ^9-THC from hemp oil cosmetics was conducted to address concerns about Δ^9-THC in cosmetics (Pless and Leson 2001). The results strongly suggested that even unrealistically extensive use of such products could not result in positive screening or confirmed urine tests for marijuana.

CLOSING STATEMENTS

Antibacterial activity of hemp and other fibre plants has been reviewed. The review suggests that natural fibre plants could serve as a potential source of antibacterial components and can be utilized effectively without being wasted. Cannabinoids, alkanoids, other bioactive compounds or phenolic compounds of lignin may contribute to the antibacterial character of hemp. Recently, a series of tests has been conducted on hemp hurd for its antibacterial activity (not published yet), and strong antibacterial activity is shown against *E. coli*. This finding reveals tremendous opportunity of hemp hurd to be used in functional applications. Intensive research is needed towards identification of active compounds for antibacterial effect and utilization of inexpensive materials in value-added diversified products with consideration into their antibacterial performance. Future work should focus on the development of new antimicrobial polymer composites to be used where contamination by microorganisms is of concern. Participation and collaboration of research institutes, industry, and government regulatory agencies will be the key for the success of antimicrobial polymer composites.

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3. CONCEPTUAL FRAMEWORK AND METHODOLOGY

Plastics, paper, glass and metals are prevalent as traditional food packaging materials, while plastics hold the highest market share of 37% by value. However, environmental sustainability is driving an ever increasing demand for exploring alternatives to traditional plastics for food packaging. The key motivation of this research was to develop a sustainable alternative material for food packaging application.

3.1 Conceptual framework

The overall objective was to develop an antibacterial biocomposite from biobased material for food packaging and successfully accomplished in 4 steps described below.

Step 1: Selecting bioplastic

Poly(lactic acid) (PLA) is acknowledged as an important biodegradable polymer for industrial plastic applications because of its versatility in processability and potential biodegradability. However, apart from the high cost, a major shortcoming of PLA is a slow recrystallization, and hence often requiring an added nucleating agent. The inclusion of a lignocellulosic fillers, such hemp hurd (HH), in PLA are able to assist to achieve favourable crystallization kinetics acting as a nucleating agent.

Step 2: Incorporating biobased filler in PLA

Biobased fillers are added to polymers to lower their overall material cost. Industrial hemp fibres are used as a composite reinforcement because of their high specific mechanical properties, however, hemp hurd, a co-product of the hemp fibre production as a biobased filler is relatively unexplored. The application of industrial hemp hurd (HH) as a filler for biocomposites not only strengthens the value chain, but also addresses environmental concern associated with plastic recycling.

Step 3: Using compatibilizer at address incompatibility of PLA and HH

Interfacial adhesion between natural fibres and polymer matrix is the key issue in terms of overall performance, since it dictates the resultant properties of the biocomposites. To improve interfacial adhesion, a compatibilizer is often compounded with thermoplastics, specifically PLA for biocomposite utilization. The effectiveness of GMA as compatibilizer in HH/PLA biocomposite is a relatively unexplored research question. To that end, this study analyses HH as value-added filler for PLA grafted with GMA in the form of an engineered biocomposite.

Step 4: Developing antibacterial biocomposite

The application of an antimicrobial agent to the biocomposite packaging material can delay or even prevent the growth of microorganisms on the product surface and, hence, lead to an extension of the shelf-life of food. Silver in nanoparticle form are regarded as a highly effective antibacterial agent. In this research, a silver nano-additive antibacterial agent was synthesized and loaded into the HH filler (AgNP-HH) using a proprietary method developed in collaboration with Ecofibre Industries Operations Pty Ltd.

Then, an antibacterial biocomposite was produced using extrusion/injection moulding with silver nanoparticles (AgNPs) encapsulated in HH filler, and PLA as the polymer matrix, grafted with GMA as a polymer/filler interfacial compatibilizer. Initially, the technical viability was analysed through investigations of mechanical, thermal, antibacterial and migration behaviour of the biocomposite. Then, financial aspects of the developed antibacterial biocomposite were assessed by applying the economic analysis tool (cost benefit analysis) for determining the potential of the biocomposite for food packaging in Australia.

A conceptual frame work of this study based on the prior discussion is depicted in Figure 1.

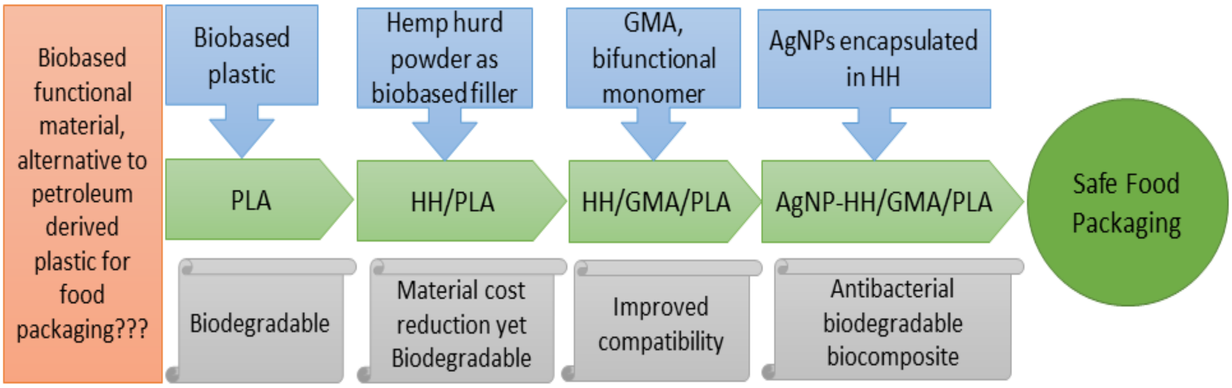

Figure 1. Conceptual framework for material development

3.2 Methodology

The undertakings to meet the objectives of this research are shown in Figure 2.

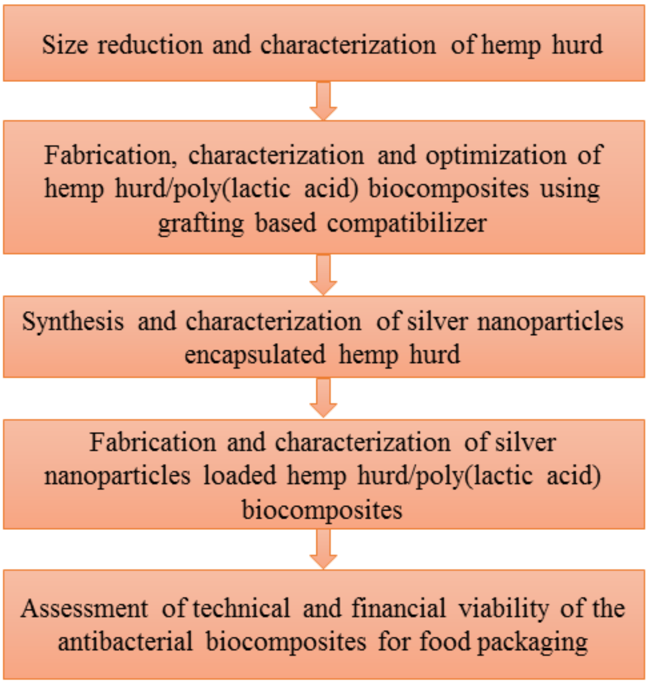

Figure 2. A Flowchart of methodology of this thesis

To address the objectives of the research project, the following methods were used:

- Size reduction of HH chips using a cutter mill and a rotary mill followed by different size of sieves to achieve desired particle sizes appropriate for compounding with a polymer using extrusion and injection moulding
- Fabrication of HH/PLA biocomposites by extrusion and injection moulding through utilization of grafting-based interfacial compatibilization that will reduce the incompatibility between the PLA and HH particles
- Investigation of the effect of HH and compatibilizer on the physical, mechanical and thermal properties of biocomposites to benchmark the material against commercially available products
- Synthesis of AgNPs encapsulated in HH using a proprietary method developed in collaboration with Ecofibre Pty Ltd to produce the nanoparticles and load on to the HH in a single step
- Fabrication of biocomposites with AgNPs loaded HH filler and polylactide as the polymer matrix grafted with GMA compatibilizer to obtain antibacterial biocomposites

- Characterization of raw materials and biocomposites using laser diffraction particle size analyser, X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), inductively coupled plasma optical emission spectrometry (ICP-OES) and antibacterial resistance against gram negative *E. Coli*
- Assessment of financial viability of the biocomposites as food packaging material using cost benefit analysis tool

In the following section, the materials and characterization techniques used in this study to achieve the ultimate goal have been discussed.

3.2.1 Materials

Commercial PLA (Grade 4032D) pellets were purchased from NatureWorks, LLC. (Minnetonka, MN) as they are compatible in extrusion and injection moulding process.

Three types of HH (retted, semi-retted, and non-retted) were used in this study. Semi-retted and non-retted hemp hurd was obtained from Ecofibre Industries Operations Pty (Australia). Retted HH powder was received from Research Centre of China-Hemp Materials, Beijing, China.

GMA, as the compatibilizer, and tert butyl perbenzoate (TBPB), as the initiator, were supplied by the Ningbo Institute of Industrial Technology and were used with no further purification.

The silver nanoparticles were synthesized and loaded into HH filler in a single stage using a proprietary method developed in collaboration with Ecofibre Pty Ltd.

3.2.2 Size Reduction of Hemp Hurd and Biocomposite Fabrication

Size reduction of hemp hurd was necessary prior to be compounded with PLA using extruder. For this purpose, two successive mills were used. A cutter mill was used for chopping hemp hurd chips into approximately 1 mm snippets. Then, the snippets were repeatedly passed through a rotary mill to be milled at desired particle size. Different size of sieve was used to separate the hemp hurd powder into appropriate particle sizes.

PLA and HH were vacuum-dried at 85°C for 12 h to eliminate moisture and water content. Then, they were melt-blended using a twin screw extruder to obtain homogenously mixed pellets. The extruded pellets were subsequently moulded as standard test bars using an injection moulding machine for further characterization.

3.2.3 Characterizations and Analysis

The following methods/techniques were used for the characterization and analysis of raw materials, processed materials and biocomposites to understand material behaviour and characteristics. They are well the established methods used in material characterization in material engineering.

Thermal Analysis

The thermal properties of the biocomposites were characterized using differential scanning calorimetry (DSC) on a DSC analyser to understand crystallization kinetics and associated properties such as glass transition temperature, crystallization temperature and melting temperature. The samples were stabilized at 30ºC for 1 min before they were heated to 200ºC at 10ºC/min, and maintained at 200ºC for 3 min to erase thermal history prior to cooling down to 30ºC at 25ºC/min. After 1 min at 30ºC, the second scan from 30ºC to 200ºC at 10ºC/min was performed. Throughout the whole process, the sample cell was kept under a nitrogen flow of 20 mL/min. This analysis provided understanding of crystallization kinetics

Thermogravimetric analysis (TGA) tests were used to evaluate thermal stability and carried out by TGA analyser at a linear heating rate of 10°C/min under nitrogen atmosphere. It provided decomposition behaviour of the materials as a function of increasing temperature. The range of temperature was from 25°C to 550°C. The weight of samples was kept at 3 mg to 5 mg. Differential TG curves (DTGA) were obtained from the first derivative of TGA data.

Chemical Analysis

Fourier transform infrared (FTIR) spectra of samples prepared with KBr were recorded by a spectrophotometer with a resolution of 4 cm^{-1} and 32 scans in the range 4000 to 400 cm^{-1} to identify any changes in chemical bonding between materials. To prepare samples, approximately 3 mg of blends were crushed into fine particles and mixed with about 15 mg KBr and then pressed into a pellet for FTIR measurement.

Crystalline Structure Analysis

Wide-angle X-ray diffraction (WAXD) analysis was performed on a D8 Advance diffractometer with a $Cu\ K_\alpha$ radiation (λ_x= 0.154 nm) to identify crystalline structure of the materials. The equipment was operated at 40 kV and 40 mA under ambient temperature. The scan range was between 5° and 90° with a scan of 3.5°/min.

Microstructural Observations

The morphologies were studied by scanning electron microscopy (SEM) images. The samples were sputter gold-coated for 120 s and were examined in a SEM operated at 10 kV with use of the secondary electron signal.

Particle Size Analysis

Particle size distribution was measured using a laser diffraction particle size analyser.

Mechanical Property Measurements

An Instron 5567 was used for the tensile properties measurements according to the GB/T 1040.1-2006 standard and flexural properties according to ISO 178: 2010 standard. The standard bar-shaped samples were used to determine the tensile and flexural properties which were prepared using a plastic injection machine. Impact testing was performed according to ISO179-1: 98 using a mechanical impact tester.

Antibacterial Test

The antibacterial performance of hemp hurd and biocomposites were tested on *E. coli* (ATCC # 25922), which is a common strain used for antibacterial testing. Antibacterial performance was investigated according to ASTM E2149-10 to ensure efficient interaction between bacteria and biocomposite in the test.

Heavy Metals Migration Test

Heavy metals migration from the biocomposites was measured according to Council Directive 82/711/EEC published by European Commission in 1982. 3% (v/v) aqueous acetic acid and 95% (v/v) aqueous ethanol were selected as food simulants, which simulates all alcoholic, aqueous, and acidic foods, albeit at a higher concentration of the alcohol, which is specified at 10 % (v/v) in the standard. An inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine element migration behaviour of the biocomposites in the stated food simulants.

4. PUBLICATIONS FORMING MATERIAL DEVELOPMENT AND PROPERTIES ANALYSIS

4.1 Paper-III: Antibacterial Properties of Hemp Hurd Powder against *E. coli*

Khan, B. A, Wang, J., Warner, P and Wang, H. (2015). Antibacterial Properties of Hemp Hurd Powder against *E. coli*. Journal of Applied Polymer Science, Vol. 132, Issue 10

The objective of this article was to critically analyse hemp hurd focusing on antibacterial efficacy. Size reduction of hemp hurd was carried out using a cutter mill followed by a rotary mill to achieve desired particle size. Morphologies of hemp hurd were studied using scanning electron microscopy, thermal decomposition behaviour was observed using thermogravimetric analysis and antibacterial property was tested against *E. coli* according to relevant ASTM standard. The overall contribution of this article in this thesis is to provide in depth understanding on potential application of hemp hurd as a biobased antibacterial filler and a carrier vehicle of an antibacterial agent in biocomposites.

JOURNAL OF Applied Polymer SCIENCE

Antibacterial Properties of Hemp Hurd Powder Against *E. coli*

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ABSTRACT: Hemp (*Cannabis sativa L.*) is an eco-friendly and multifunctional plant. Hemp hurd is a by-product of hemp plant during hemp fiber separation. Although hemp hurd is repeatedly announced owing antibacterial activity, it has never been systematically investigated and reported. In this study, the antibacterial activity of hemp hurd powder against *Escherichia coli* is investigated. This article reveals antibacterial activity of hemp hurd where hemp hurd powder inhibits the growth of *E. coli*. Meanwhile, the self-contamination (forming during retting process) inside hemp hurd has dramatic impact on the antibacterial performance. To achieve better antibacterial activity, hemp hurd was heat treated to eliminate self-contaminations. The impact of the particle sizes and heat treatment on the antibacterial effectiveness was evaluated. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41588.

KEYWORDS: biomaterials; biomedical applications; morphology; properties and characterization; thermogravimetric analysis (TGA)

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INTRODUCTION

Botanically, hemp is a member of the most advanced plant family on earth. It is a dioecious woody, herbaceous annual plant that uses the sun more efficiently than any other plants and it can be grown in virtually any climate or soil condition. Hemp has a long history of cultivation for a variety of applications including textiles, medicine, recreational drugs, and food.[1,2] Hemp can be divided into fiber type (industrial hemp), intermediate type, and drug type (known as marijuana), with tetrahydrocannabinol (THC) content ranging from <0.3%, 0.3–1.0%, and 1–20%, respectively.[3,4]

Industrial hemp is a kind of yearly harvested plant where hemp fiber is the main product of its cultivation. Hemp hurd (also called hemp core) is a by-product and agricultural waste of hemp plant. It is a residue from the hemp stem after the bast fibers are removed for textile. Hemp hurd is mostly used for animal bedding because of its favorable properties: good absorbency, easy handling, and rapid composting after use.[5] Another application of hemp hurd is in construction sector. New utilizations of the hemp hurd are under development,[6] however, a great amount of hemp hurd (accounting for 70–80% of the hemp stem) is disposed by combustion or landfilling, which results in resource waste. To develop its utilizations, hemp hurd could be milled into powder. For instance, hemp hurd powder is a good filler in hemp-reinforced plastic composites.[7] Also, hemp hurd powder can be incorporated in 3D printing filament material in the emerging 3D printing technology.[8] Hemp hurd powder may also be applied to produce activated carbon with high specific surface areas, micro-porous structure, high adsorption capacity, and degree of surface reactivity.[9]

Recently, hemp as an antibacterial agent has been attracting more and more attention.[10,11] Hemp fiber has been confirmed with excellent antibacterial activity, which leads hemp fiber to be a good material for functional textiles.[12] However, antibacterial performance of hemp hurd has never been systematically investigated, although it is repeatedly announced that hemp hurd also has similar property.[13] The antibacterial properties in hemp hurd may come from cannabinoids, alkanoids, other bioactive compounds, or compounds of lignin.[11,14]

In this study, hemp hurd was milled into powder with different size. Then the antibacterial properties against *Escherichia coli* were investigated. The impact of retting process and particle size of hemp hurd powder on the antimicrobial performance was studied. Due to huge amount of hemp hurd waste every year, these observations may stimulate future inclusion of hemp hurd in antibacterial food package, hence utilize agricultural waste resource and reduce environmental pollution.[15]

MATERIALS AND METHODS

Material

Three types of hemp hurd (retted, semi-retted, and non-retted) were used in this study. Semi-retted and non-retted hemp hurd was obtained from Ecofibre Industries Operations Pty (Australia). Retted hemp hurd powder was received from Research

Table I. Retting Status and Particle Size of Hemp Hurd

Retting status	Mean particle size
Semi-retted	188.4 μm
	85.4 μm
	44.3 μm
	21.2 μm
Non-retted	204.0 μm
	99.8 μm
	47.2 μm
	20.5 μm
Retted	37 μm
	19.1 μm

Centre of China-Hemp Materials, Beijing, China. Retted hemp hurd was obtained at about 20°C for 8 days in dewing process. Semi-retted hemp hurd was achieved at about at 20°C for 3 days followed by mechanical separation. For the non-retted hemp hurd, it was separated through mechanical decortication.

A cutter mill (Pulverisette 19 from Fritsch Gmbh, Germany) was used for chopping hemp hurd chips into approximately 1 mm snippets. Hemp hurd snippets were passed through a rotary mill (Pulverisette 14 from Fritsch) to be milled repeatedly up to 55 times to obtain desired particle size. Different size of sieve was applied to separate the hemp hurd powder into different particle sizes.

Particle size distribution was measured using a Mastersizer 2000 (Malvern Instruments, UK) fitted with Hydro 2000S. The dispersion medium was deionized water.[16] Table I shows the particle size of the different retted samples with various time of milling. All results were presented according to a volume-based particle size distribution.

Antibacterial Test

The hemp hurd powder was tested for its antibacterial performance against *E. coli* (ATCC25922). The bacterial cultures were maintained on nutrient agar slopes. They were grown in sterile Tryptic Soy Broth and incubated at 37°C for 18 h. Working buffer solution (0.3 m*M* KH_2PO_4) was adjusted pH to 7.2 ± 0.1 with a dilute solution of NaOH, and then capped, sterilized, and stored at room temperature.

To prepare the working bacterial dilution, the culture was diluted with the sterile buffer solution until the solution has an absorbance of 0.28 ± 0.02 at 475 nm (as measured spectrophotometrically), which corresponds to a concentration of 1.5–3.0 $\times 10^8$ colony forming units per milliliter (CFU/mL). The Atherton cyber series autoclave was used for sterilization and media preparation at 121°C for 20 min.

Antibacterial performance of the hemp hurd powder was investigated according to ASTM E2149-10, described as the following: (1) 1.0 g of hemp hurd powder was placed into a 250-mL flasks with 50 ml working bacterial dilution; (2) the flask was shaken on an agitation shaker at a speed of 300 rpm at 25°C for 1 h ± 5 min; (3) 1 mL of the solution before or after shaking was inoculated on a plate containing 15 mL tryptic soya agars; (4) the inoculated plate were cultivated at 37°C for 24 h; and (5) active bacteria were counted and antibacterial effect was calculated. Percent reduction of the organisms resulting from treated sample directly compared to "inoculum only" sample after specified contact time is calculated. Results are presented in percent reduction by counting CFU/mL of bacteria.

Heat Treatment and Thermogravimetric Analysis

To study whether the antibacterial property in the hemp hurd can be preserved after hemp hurd powder being processed at different processing temperature, hemp hurd powder was heated at 80, 120, 140, and 160°C for 0.5–3 h in a dry oven. Hemp hurd powder was kept open in a ceramic beaker to allow the evaporation of moisture from the material.

Thermogravimetric analysis (TGA) was used to determine the thermal stability of the hemp hurd powder. The constituents of hemp hurd powder have different thermal reactivity and decomposition at different temperatures. TGA analysis on hemp hurd powder was carried out by a thermal gravimetric analyzer (TGA Q500). In ramp method, the samples were heated from 10°C to 400°C at a rate of 20 °C/min. In ramp and isothermal method, the sample was heated up to 100°C at a rate of 20 °C/min and held for 20 min, then it was heated up to 160°C at a rate of 20 °C/min and held for another 20 min. Experiments were carried out in a nitrogen medium (60 mL/min) and the weight was recorded as a function of increasing temperature.

Morphologies

The morphologies of milled hemp hurd powder were studied by scanning electron microscopy (SEM) images. The samples were sputter gold-coated for 120 s and were examined in a JEOL JCM 6000 SEM operated at 10 kV with use of the secondary electron signal.

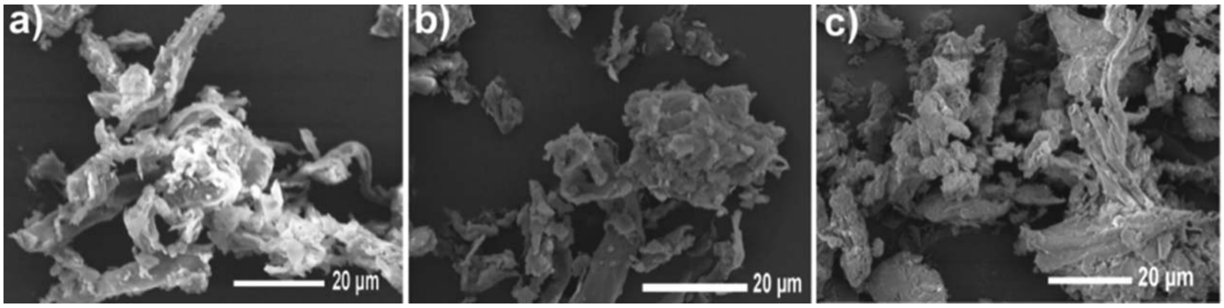

Figure 1. SEM images of hemp hurd powder: (a) retted; (b) semi-retted; (c) non-retted.

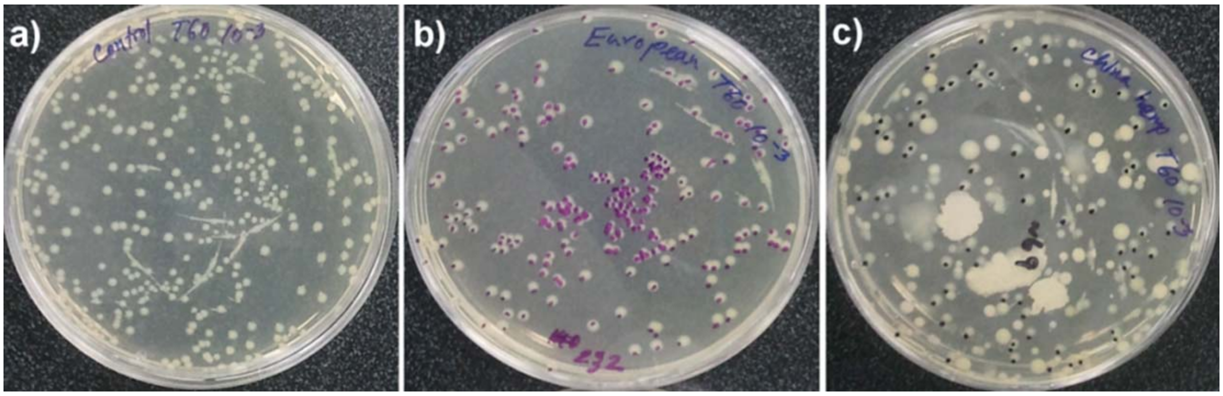

Figure 2. Inhibition of bacterial growth of hemp hurd powder: (a) control; (b) non-retted hemp hurd powder; (c) retted hemp hurd powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Morphologies

Figure 1 shows the SEM image (High-vac, 10 kV) of hemp hurd powder. A number of thin hemp hurd slices and irregular-shaped aggregation were clearly observed. In addition, some short fibers still existed because of insufficient pulverization.[17] In general, it shows an irregular rough surface with sharp edges and grooves. The hemp hurd powder shows the porous structure, indicating low bulk density and high water absorption capacity. The high surface roughness of the hemp hurd powder ensures a good bond with the polymer matrix, so that the hemp hurd powder will be able to be applied to reinforced plastic and other composites.

Inhibition of Bacterial Growth

The antibacterial activity of hemp hurd powder is presented in Figure 2. It is evident that the hemp hurd powder inhibited the growth of *E.* coli as the plates of control and the hemp hurd powder have shown different appearance in the bacterial lawn. The controlled sample has the CFU 340; while the non-retted hemp hurd powder CFU reduces 30% to 235; and the retted hemp hurd powder CFU decreases 78% to 75. These results demonstrate that retted hemp hurd is more effective for the inhabitation of *E. coli* bacteria. However, in the petri dish, there are still some other types of microorganisms remaining in both retted and non-retted hemp hurd powder (although only *E. coli* was expected). These contaminations are from hemp hurd powder itself, and they might have occurred from the fields where they grow up and existed during fiber processing (retted or non-retted). It is also notable that retted hemp hurd embraced more severe contamination than the non-retted hemp hurd.

The retting process is a controlled degradation of plant stems to allow the fiber to be separated from the woody core (hurd). Dew, water, enzymatic, mechanical, and chemical retting processes are common for hemp.[18,19] Therefore, the retting process of hemp provides more opportunity for hemp hurd to be contaminated and promulgated.

Self-Contamination of Hemp Hurd

To remove self-contaminations, retted hemp hurd powder was treated in the air oven at 180°C for 20 min. Figure 3 shows the antibacterial performance of retted hemp hurd powder before and after heat treatment. It is clearly observed that self-contaminations are eliminated after heat treatment. Compared with the non-treated hemp hurd powder having around 78%

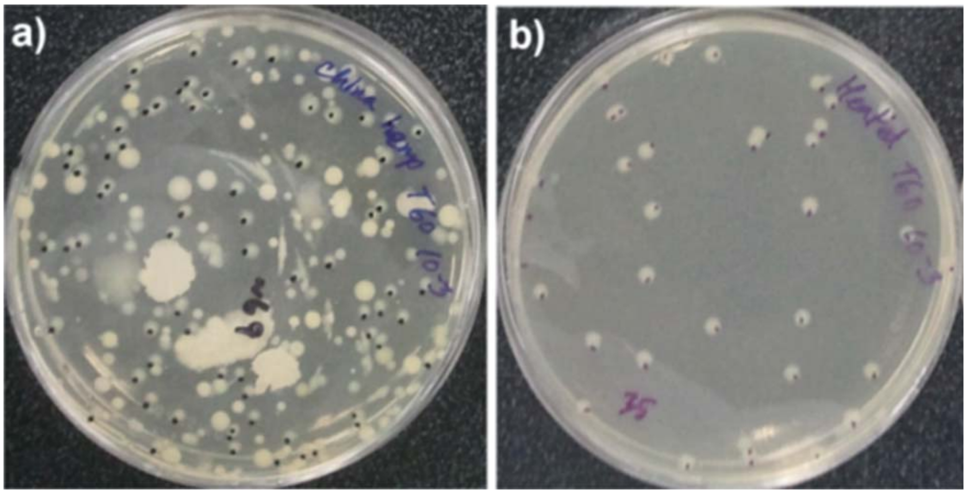

Figure 3. The antibacterial activity of retted hemp hurd: (a) before and (b) after heat treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

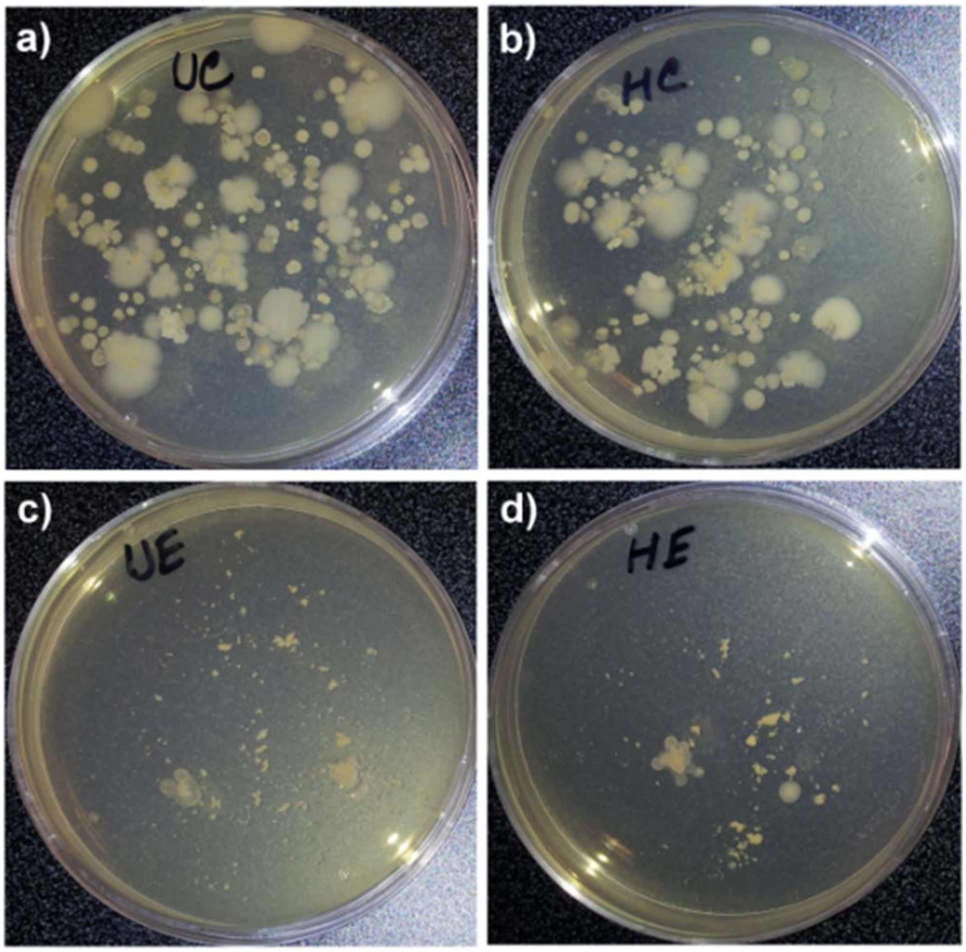

Figure 4. Status of self-contaminations: (a) retted hemp hurd powder without heat treatment; (b) retted hemp hurd powder treated at 80°C; (c) un-retted hemp hurd powder without heat treatment; and (d) un-retted hemp hurd powder treated at 80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reduction in CFU, the heat treated hemp hurd powder had more efficient antibacterial activity with 90% reduction in CFU. Therefore, to achieve the best performance, the elimination of self-contamination is certainly important. Inactivation of micro-organisms (such as bacteria) can be achieved by chemical and/or physical means, such as heat, chemical solutions, gases, and radiation.[20–22] It has been confirmed that heat has detrimental effects on living cells,[20] and the heat-based sterilization techniques were developed and commercially used to dispel undesired medium preservation.[23]

Table II. Observation on Elimination of Self-Contaminations After Heat Treatment

	120°C	140°C	160°C
30 min	×	×	×
60 min	×	×	√
90 min	×	√	√
120 min	×	√	√
150 min	×	√	√
180 min	√	√	√

(×) = contamination remaining; (√) = contamination completely eliminated.

To obtain appropriate and effective contamination elimination, different heat treatment was investigated in this study. Hemp hurd powder was kept in the oven at 80°C for more than 3 h until all the moisture was completely removed. Then, the powder was spread on agar containing petri dishes and incubated at 35 ± 2°C for 24 h. Figure 4 shows the effect of low temperature treatment to eliminate the self-contaminations, presenting that

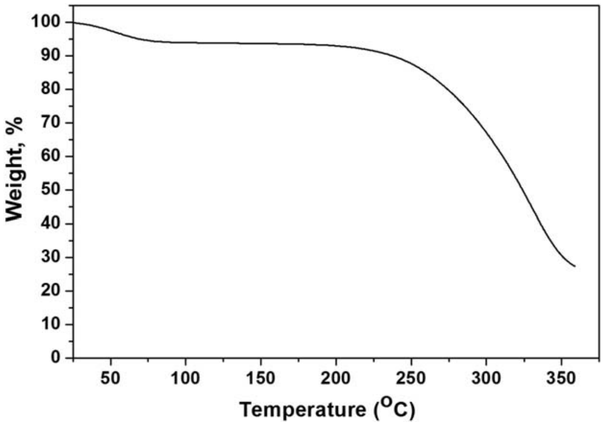

Figure 5. TGA curves of retted hemp hurd.

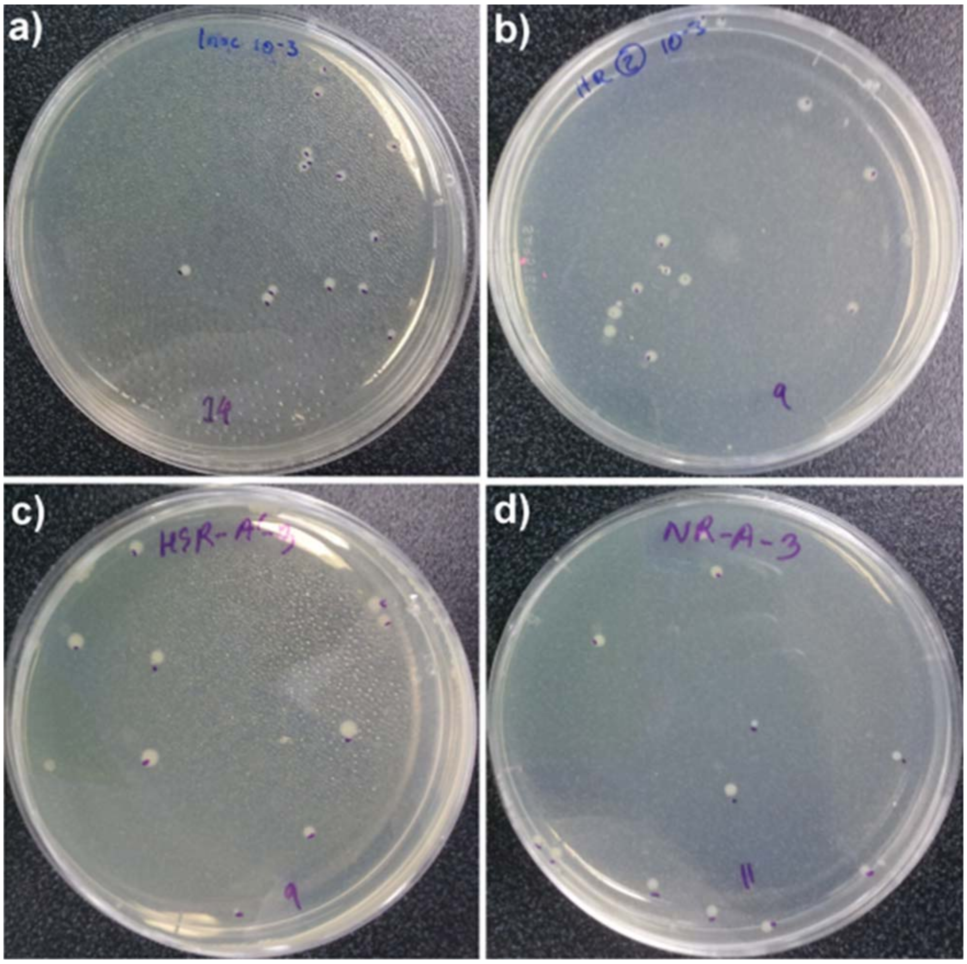

Figure 6. Antibacterial activities of different types of hemp hurd powder (20 μm): (a) control; (b) retted hemp hurd powder; (c) semi-retted hemp hurd powder; and (d) non-retted hemp hurd powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

heat treatment at 80°C for 3 h was not sufficient to eliminate the existing contaminations of hemp hurd powder. This is due to the higher decomposing temperature of some contaminations.[24] Dew, water, enzymatic, mechanical, and chemical retting processes are common for hemp. Therefore, the retting process of hemp provides more opportunity (along with the favorable condition for bacterial growth) to hemp hurd to be contaminated and promulgated. It is necessary to remove those contaminations for further antibacterial application.

To investigate heat-based conventional sterilization methods, both moist heat and dry heat were studied. In the case of moist heat in an autoclave, a temperature of 120°C at a pressure of 15 psi was applied for 20 min, while dry heat sterilization was proceeded at 170°C for 1 h.[23] To study the impact of temperature and holding time on the self-contamination elimination in hemp hurd powder, a series of experiments were carried out, and the status of self-contaminations was observed by simply spreading out heat-treated hemp hurd powder on the agar containing petri dish, followed by incubating at 35 ± 2°C for 24 h. Table II summarizes the contamination status at different heat-curing conditions, indicating that the higher the curing temperature, the shorter the curing time to eliminate self-contaminations.

Thermal Degradation

TGA was applied to study the weight loss of hemp hurd powder with the increase of temperature. The degradation process was divided into four stages: moisture evaporation, hemicellulose degradation, cellulose degradation, and lignin decomposition. Moisture is present in the material in two forms: free water and linked water. Free water is attached on the fiber surface and evaporates at lower temperature (25–150°C). The linked water with the hydroxyl groups is bonded in hemicellulose and lignin, and decomposes at higher temperatures.[25] After the removal of free water, the degradation process begins in the cellulose, hemicellulose, lignin constituents, and the associated linked water.[26,27] TGA curves in Figure 5 suggest that at 160°C, no thermal degradation will occur to the hemp hurd powder itself.

Effect of Particle Size and Temperature

Retted (37 μm, 19.1 μm), semi-retted (188.4 μm, 85.4 μm, 44.3 μm, 21.2 μm), and non-retted (204 μm, 99.8 μm, 47.2 μm, 20.5 μm) hemp hurd powder of different particle sizes were investigated for antibacterial activity. Heat treatment (160°C for 2 h) was carried out to remove self-contaminations before testing. Particle size did not show any effect on antibacterial activity, and 2-h contact time was sufficient for both fine and coarse particle to present maximum antibacterial activity. Figure 6 shows antibacterial result of selected hemp hurd powder, where both retted and semi-retted hemp hurd were heat-treated, and non-retted hemp hurd was applied without further treatment due to non-contaminations. Figure 6(a) is the control without any hemp hurd powder, and Figure 6(b–d) contain hemp hurd powder. All the three types of hemp hurd powder show similar antibacterial activity, which further confirmed that self-contaminations in hemp hurd are the main impact factor on the antibacterial performance.

Potential Applications and Future Work

There is a great concern of contaminations by microorganisms in a variety of areas, for example, medical devices, healthcare products, water purification systems, hospitals, dental office equipment, food packaging, food storage, and household sanitation.[28] One possible way to address microbial contamination is to develop materials with antimicrobial properties.[29]

Polymers such as polyethylene, polyurethane, polytetrafluoroethylene, polyacetal, polymethylmethacrylate, polyethylene terepthalate, silicone rubber, polysulfone, polyetheretherketone, poly(lactic acid), poly(glycolic acid), and so on, are used in various biomedical fields.[30] Incorporating antibacterial hemp hurd powder as filler in the polymer composites could provide not only lighter weight but also protection against bacterial attachment. Hemp hurd reinforced polymer composites could be an excellent choice for prostheses. Similarly, hemp hurd powder can be incorporated in food packaging composites, and be considered as eco-friendly. Hemp hurd powder incorporated polymer composites formed by injection molding can provide packaging materials with a wide range of shape and sizes for containing a range of foods including meat, salads, and ready-made food products.

CONCLUSION

In this study, the antibacterial activity of hemp hurd powder against *E. coli* was systematically studied by applying different hemp hurd powder (retted, semi-retted, and non-retted) with different size. To apply the retted and semi-retted hemp hurd powder as antibacterial materials, it is necessary to eliminate contaminations that come from external surroundings (such as humid and temperature) during retting process. The heat-treated hemp hurd powder at 160°C for 2 h showed efficient antibacterial activity up to 90% reduction in CFU. It was also explored that the particle size of hurd powder has no obvious impact on the antibacterial performance. It is proposed that the hemp hurd powder has many potential applications in biomedical, food packaging, polymer composites, and other value added diversified products.

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4.2 Paper-IV: Methacrylate-Compatibilized Poly(lactic acid)/Hemp Hurd Biocomposites: Processing, Crystallization, and Thermo-mechanical Response

Khan, B. A, Na, H., Chevali, V. S., Zhu, J., Warner, P and Wang, H. (2016). Glycidyl Methacrylate-Compatibilized Poly(lactic acid)/Hemp Hurd Biocomposites: Processing, Crystallization, and Thermo-mechanical Response. *In Submission*

The objective of this article was to produce biocomposite with poly(lactic acid) as matrix and hemp hurd as biobased filler. The interfacial compatibility was improved by using glycidyl methacrylate grafting base compatibilizer. The characterization results of the developed biocomposites were encouraging. The biocomposites possess the potential to be cost-competitive, and be durable in service and biodegradable post-service, hence valuable for packaging and disposable goods applications that require dimensional and thermal stability. The overall contribution of this article in this thesis is to provide understanding addressing the incompatibility issue associated with poly(lactic acid) and hemp hurd.

Glycidyl Methacrylate-Compatibilized Poly(lactic acid)/Hemp Hurd Biocomposites: Processing, Crystallization, and Thermo-mechanical Response

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Abstract:

A biocomposite was developed with hemp hurd (Cannabis sativa L.) and poly(lactic acid) with properties comparable to poly(lactic acid) with grafting-based interfacial compatibilization. Poly(lactic acid) was extruded with hemp hurd and glycidyl methacrylate as the polymer/hurd interfacial compatibilizer, and injection molded. Interfacial compatibility between poly(lactic acid) and hemp hurd increased with grafted glycidyl methacrylate in comparison to the non-compatibilized control, as corroborated by scanning electron microscopy fractography. The mechanical properties showed increases in the glycidyl methacrylate-grafted hemp hurd/poly(lactic acid) biocomposite, retaining 94% of the neat polymer strength, with increases in crystallinity at 20% (w/w) loading of hemp hurd.

Keywords: *Hemp Hurd; Poly(lactic acid); Glycidyl Methacrylate; Biocomposite; Injection Molding; Mechanical Properties*

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1 Introduction

Polylactic acid (PLA) or poly(2-hydroxypropionic acid) is an aliphatic polyester[1] synthesized from renewable resources and produced with a capacity of over 140,000 tons per year[2], with usage estimated to reach 2 million tons by year 2020[3]. PLA is recognized as a key biodegradable polymer[4] for industrial plastic applications because of its versatility in processability[5]. PLA is an effective bio-based alternative of polyethylene terephthalate because of similar mechanical properties[6]. Bioplastics such as PLA are utilized as matrices in sustainable biocomposites with considerable research effort devoted to the development of eco-friendly, sustainable bio-products, including biocomposites[7] applications for packaging, automotive, building, and appliance industries, and feedstock for 3D printing[8]. Sustainable industrial products manufactured from renewable resources with recycling capability and triggered biodegradability[9,10] are necessitating the exploration of novel biomass fillers for development for biocomposites, with commercial viability and environmental acceptability[11].

Apart from the high cost, the major shortcomings of PLA in its unfilled form are the moderate to low mechanical and thermal stabilities[12] for biocomposite applications. Heat resistant PLA plastic products often require injection molding with rapid recrystallization, and hence require an added nucleating agent[1]. Inclusion of microscale additives such as talc[13], cellulose fibers[12] and wood fibers[14–17] in PLA is a common practice to achieve favorable crystallization kinetics. The key benefits of using PLA are its higher mechanical properties, albeit with lower elongation-to-failure and high raw material cost, in comparison to commodity thermoplastic polymers such as polyolefins. Despite efforts to improve cost-effective production of PLA[1], the current cost remains higher than the cost of polyolefins, affecting its competitiveness. Increased production volumes of PLA and the determinate nature of petroleum reserves are intensifying PLA-based biocomposite development to petrochemical-derived plastics and composites available in the market.

The development of sustainable, thermally/mechanically durable biocomposites with PLA and biomass-derived lignocellulosic natural fibers and fillers[18] is receiving attention recently as this combination (a) increases the mechanical/thermal stability[19], (b) preserves or enhances biodegradability[20], and (c) increases the cost-to-performance ratio[21]. The major constituents of plant-based lignocellulosic fibers and fillers are cellulose, hemicellulose, and lignin, whose composition varies depending on their origin, species, age, and retting process. The commercial development and industrial usage of these plant-based fibers/fillers are a function of the turnaround in harvest time and consistent fiber quality. The chemical constituents and complex chemical structure of plant-based fibers affect their properties. Of particular interest is the industrial hemp plant, whose production yields a large fraction of biomass without a period of dormancy that is common with many cash crops[22]. In the hemp fiber production, decortication of the hemp stems provides two biomass products, i.e., the hemp fiber and hemp hurd (HH). The hemp bast fibers are used as reinforcement or textiles and exhibit potential as a composite reinforcement[23] because of their high specific mechanical properties. HH is the woody core of the stem (approximately 70% of the stem mass)[24], which is used in applications such as animal bedding or as hempcrete for construction[25]. HH is used as a multipurpose precursor[26] and raw material that is used as a standalone filler, and in conjunction with hemp fiber for lime concrete aggregates[27], concrete mixes[28], and composites[29]. In addition, hemp hurd powder is used as a filler for interface-compatibilized rubber composites[30,31]. HH has a chemical composition similar to wood[32], albeit with greater hydrophobicity and counterintuitively, a lower adsorption potential in spite of its cellular microstructure[33]. HH and hemp fiber both are constituted by 39 - 49 wt. % cellulose and 16 - 23 wt. % hemicellulose[34], however, higher lignin content in HH is higher (~20 wt. %)[32]. However, the species of the industrial hemp plant and the sampling location of the woody HH cause a marginal variation in its structure and chemical composition[24]. Nevertheless, HH possesses an enormous potential for utilization in sustainable industrial products because of the aforementioned attributes. From economic and environmental standpoints, it is motivating to study the usage of plant co-products with HH to avoid the use of new agricultural lands, to limit competition with food products, and to offer remuneration to farmers[24].

Inclusion of HH in biocomposites for extensive industrial use can be conjectured to be beneficial if a valorization proposition can be supported. Nonetheless, the effectiveness of any novel filler for biocomposite use is dependent on effective interfacial incompatibility between hydrophilic natural fibers and hydrophobic thermoplastics, without which the weak adhesion at the two-phase interface leads to inadequate mechanical and physical properties[35], affecting mechanical strength. Thus, the critical challenge for HH to succeed as a viable filler in biocomposites with comparable properties as PLA lies in the improvement of interfacial compatibility between the two components. For this purpose, a compatibilizer is often compounded with the thermoplastics, specifically PLA for biocomposite utilization.

The addition of plant-based fillers to thermoplastic polymers entails surface modification of cellulose[36,37] and addition of compatibilizers, such as isocyanates[38] and maleated polymer[39,40] to enhance the interfacial compatibility between the polymer and the plant-based fillers. Surface modification of cellulose[36] and compatibilization, using bifunctional isocyanates[38,39,41] and maleation of PLA[40] are common practices to enhance the interfacial compatibility between the PLA and lignocellulosic fillers. Glycidyl methacrylate (GMA) is often used as a compatibilizer or coupling agent[41–44] in thermoplastics including PLA blends to improve interfacial bonding. A grafting route is used for glycidyl methacrylate (GMA)-grafted polyolefins is prepared through reactive extrusion or solution copolymerization[41,45]. Mechanical properties were significantly improved in rice-husk-filled high density polyethylene[46] and bamboo flour filled PLA composites[40,41] when GMA was used as coupling agent for these fillers whose morphology is similar to HH. Hence, the addition of a GMA in PLA/vegetal filler systems is advantageous for producing durable biocomposites.

The effectiveness of HH inclusion in GMA grafted PLA is a relatively unexplored research question. To that end, the current study analyses HH as value-added filler for GMA grafted PLA in the form of an engineered biocomposite, and reports quantitative data for future industrial product development. HH is systematically analyzed as a value-added filler for PLA to (a) maintain or exceed mechanical and thermal properties, and (b) develop a biocomposite with lower cost and comparable thermal/physical/mechanical properties as unfilled PLA through optimization of processing and properties.

2 Experimental

2.1 Polymer and Filler

Commercial PLA (4032D) was purchased from NatureWorks, LLC. (Minnetonka, MN). Retted hemp hurd powder was obtained from Ecofibre Industries Operations Pty Ltd, Australia. **Figure 1** shows the morphology of HH in the natural stalk form (Fig 3a), after extraction from the hemp stem (Fig 3b), and upon further size reduction and inspection under scanning electron microscopy (SEM) in Fig 3c-d. HH shows a unique fibrillary structure at the microscopic level, which may be investigated in future research endeavors. A cutter mill (Pulverisette 19, Fritsch Gmbh, Germany) was used for cutting HH chips into approximately 1 mm snippets, which were fed to a rotary mill (Pulverisette 14, Fritsch Gmbh, Germany) fitted with a 0.08 mm sieve, and milled to obtain the desired particle size. **Figure 2** shows the particle size distribution of HH powder, as measured through a laser diffraction particle size analyzer (Microtrac S3500). As evident from this data, variability in particle size is obtained upon size reduction, and hence a variable aspect ratio of particles is obtained. The mean particle size was 44 ± 10 μm with a maximum dimension of 400 μm.

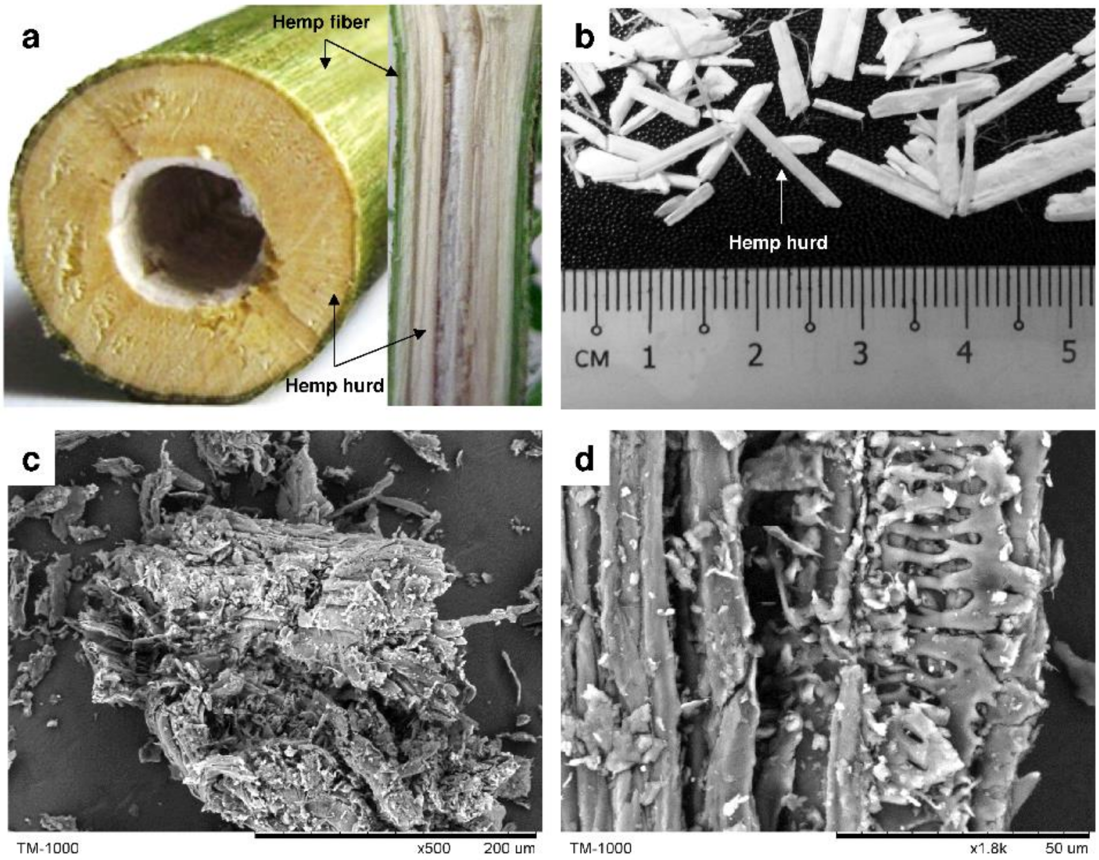


Figure 1 Morphology of hemp as (a) stem sheath, (b) chip, (c) powder, and (d) flake imaged at various observational scales.

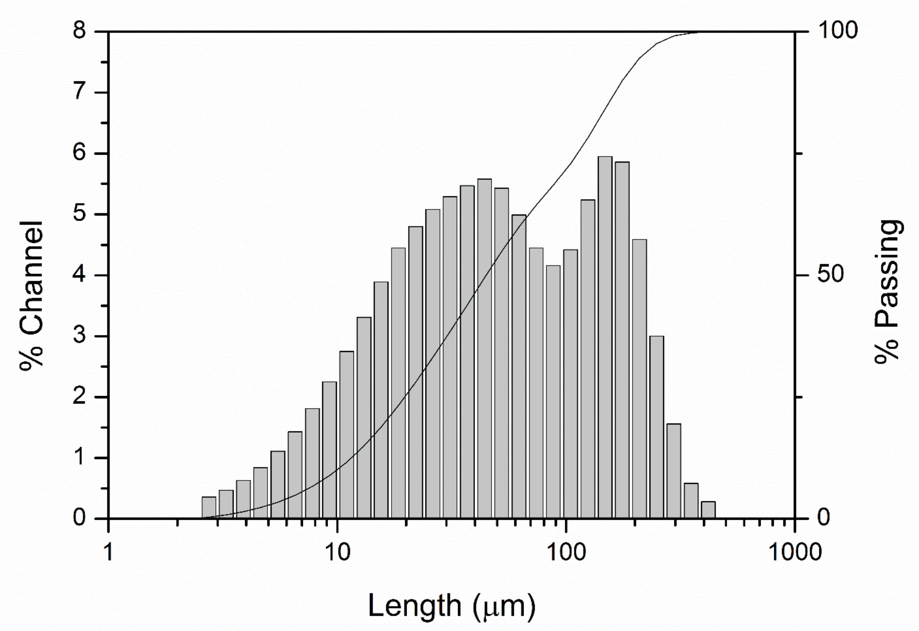
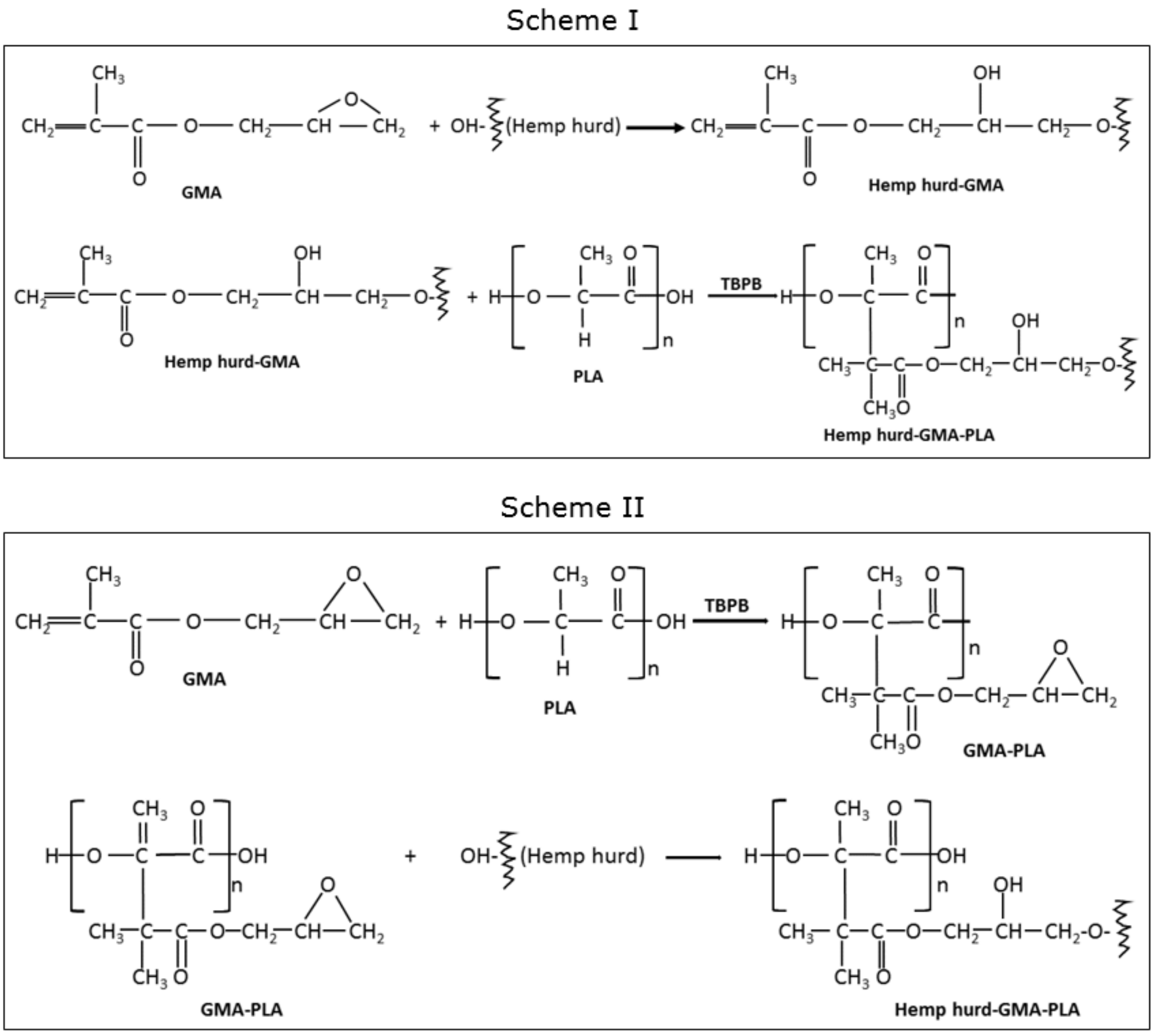


Figure 2 Particle size distribution of hemp hurd powder.

2.2 Interfacial Compatibilization

GMA and *tert*-butyl perbenzoate (TBPB), an initiator for the grafting reaction, were supplied from Aladdin Chemistry Co., Ltd. Reactive grafting method was used to graft GMA on to PLA to improve the interfacial adhesion between HH and GMA grafted PLA. GMA or 2-Oxiranylmethyl methacrylate specifically grafts on to both PLA and HH, is well understood as a bi-functional monomer containing an unsaturated group for free radical grafting on to polymeric chains. GMA contains an epoxy group that is capable of reacting with hydroxyl, carboxyl, and amine functional groups[41]. **Figure 3** shows the schematic of the grafting mechanism that progresses during melt-extrusion of the GMA grafted PLA and HH.



Scheme I

Scheme II

Figure 3 Reaction mechanism of GMA with PLA and hemp hurd using tert-butyl perbenzoate (TBPB) as an initiator.

Scheme I shows the reaction between the hydroxyl groups of HH and the epoxide ring of GMA monomer followed by the grafting onto PLA. **Scheme II** shows the GMA radical grafting onto PLA and subsequent reaction of the epoxide ring of GMA with the OH groups of HH. Thus, the GMA-grafted copolymer acts as a compatibilizing agent for reducing the interfacial incompatibility in polymer blends, and as a coupling agent in polymer matrix composites.

2.3 Extrusion and Injection Molding

Prior to processing, PLA and HH materials were vacuum-dried at 85°C for 12 h, following which pure PLA, HH/PLA, and HH/GMA/PLA were melt-blended using a lab-scale conical twin-screw extruder (Ruiming Plastics Machinery, Wuhan, China), with rotational speed of 40 rpm at 175°C for 5 min. Interestingly, minimal re-engineering in processing and tooling design is adequate to tailor the extrusion for HH/GMA-g-PLA biocomposite blends. **Table 1** shows the composition of blends prepared in this study. The extruded pellets were subsequently molded as standard test bars using a miniature injection molding machine (SZ-15, Wuhan, China). The pressure, temperature, and time were set as 3 MPa, 200°C and 30 s, respectively, and the mold temperature was maintained at 40°C.

Table 1 Composition of Fabricated Biocomposite Blends

Blend	PLA (wt. %)	HH (wt. %)	GMA (wt. %)	TBPB (wt. %)
PLA	100.0	0	0	0
PLA/HH-10	90.0	10	0	0
PLA/HH-20	80.0	20	0	0
PLA/HH-30	70.0	30	0	0
PLA/GMA/HH-10	88.5	10	1.0	0.5
PLA/GMA/HH-20	78.5	20	1.0	0.5
PLA/GMA/HH-30	68.5	30	1.0	0.5

2.4 Thermomechanical Characterization

The thermal properties of the composites were characterized using differential scanning calorimetry (DSC) on a Mettler Toledo TGA/DSC1 analyzer (Mettler-Toledo, Switzerland). The samples were stabilized at 30ºC for 1 min before they were heated to 200ºC at 10ºC/min, and maintained at 200ºC for 3 min to erase thermal history, prior to cooling down to 30ºC at 25ºC/min. After 1 min at 30ºC, the second scan from 30ºC to 200ºC at 10ºC/min was performed. Throughout the whole process, the sample cell was kept under a nitrogen flow of 20 mL/min. The glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) were determined from the second scan. T_m and T_c were taken as peak values, and T_g was taken as the midpoint of heat capacity changes. When multiple endothermic peaks were obtained, the peak temperature of the main endotherm was recorded as T_m. The crystallinity percentage (X) of PLA was calculated by using **Equation 1**.

$$X = \left(\Delta H_f - \Delta H_{cc}\right) / \left(\Delta H_f^0 w\right) \qquad (1)$$

where $\Delta H_f^0 = 93$ J/g for 100% crystalline PLA[34], ΔH_f is the enthalpy of melting, ΔH_{cc} is the cold crystallization enthalpy, and w is the weight fraction of PLA in the biocomposite.

Fourier transform infrared (FTIR) spectra of PLA or GMA-g-PLA samples prepared with KBr were recorded by a spectrophotometer (Nicolet FTIR6700 infrared spectrophotometer) with a resolution of 4 cm^{-1} and 32 scans in the range 4000 cm^{-1} to 400 cm^{-1}.

Wide-angle X-ray diffraction (WAXD) analysis was performed on a D8 Advance diffractometer (Bruker AXS) with a Cu K_α radiation (λ_x = 0.154 nm). The equipment was operated at 40 kV and 40 mA at ambient temperature. The scan range was between 2θ = 5° - 40° with a scan speed of 3.5°/min.

Thermogravimetric analysis (TGA) was used to evaluate the thermal stability on a Mettler Toledo TGA/DSC1 analyzer at a linear heating rate of 10°C/min under nitrogen atmosphere. The temperature range was 25°C to 550°C, with the mass of samples kept at 3 mg to 5 mg. Differential TG curves (DTGA) were obtained from the first derivative of the TGA data.

The morphology of the blends was imaged by a scanning electron microscope (SEM, Hitachi TM-1000) at an accelerating voltage of 10 kV. The fractured surfaces were sputtered with gold plasma prior to examination.

2.5 Mechanical Characterization

An Instron 5567 was used for the mechanical property measurements according to the GB/T 1040.1-2006 standard. The standard bar-shaped samples were used to determine the tensile strength (TS), tensile modulus, (*E*) and elongation at break (EB) on five specimens for each biocomposite were tested at a crosshead speed of 20 mm/min.

Impact testing was performed according to the ISO179-1: 98 standard. A 5.5 J pendulum was used to determine the Charpy impact strength of the bar samples (80 × 10 × 4) mm^3 with a V notch size of 2 mm depth. The impact testing was performed on five specimens for each biocomposite on a mechanical impact tester (XJ-50Z, Chengde Dahua Testing Machine Co. Ltd., Chengde, China).

The melt blends from the extruder were injected as flexural specimens according to ISO 178: 2010 standard using a miniature plastic injection machine (SZ-15, Wuhan, China). The flexural properties of the biocomposites were measured on an Instron 5567 instrument. The crosshead speed was set at 10 mm/min. The property values presented for the flexural strength and modulus are the average of five replicated tests.

3 Results and Discussion

3.1 Interfacial Compatibilization

FTIR spectra of neat PLA, neat GMA and GMA grafted PLA (GMA-g-PLA) are shown in **Figure 4**. In the neat PLA, the carbonyl stretching vibration was observed at 1755 cm^{-1}[47]. The carbonyl group in GMA and PLA showed a shift of the stretching vibration peak of the carbonyl group between 1744 cm^{-1} and 1760 cm^{-1}. The stretching vibrations of the carbon-carbon double bond of GMA[41] were observed at 1637 cm^{-1} and 944 cm^{-1}. These stretching vibrations were found to be weaker in the infrared spectra of GMA-g-PLA. The weaker intensity of the C=C suggested the number of carbon-carbon double bonds of GMA were partially expended in the grafting reaction, leading to an overall decrease in the number of double bonds. Thus, the infrared spectra of the graft copolymer (GMA-g-PLA) supported that a GMA molecule was grafted onto the C atom adjacent to the carbonyl group in the molecular chain of PLA.

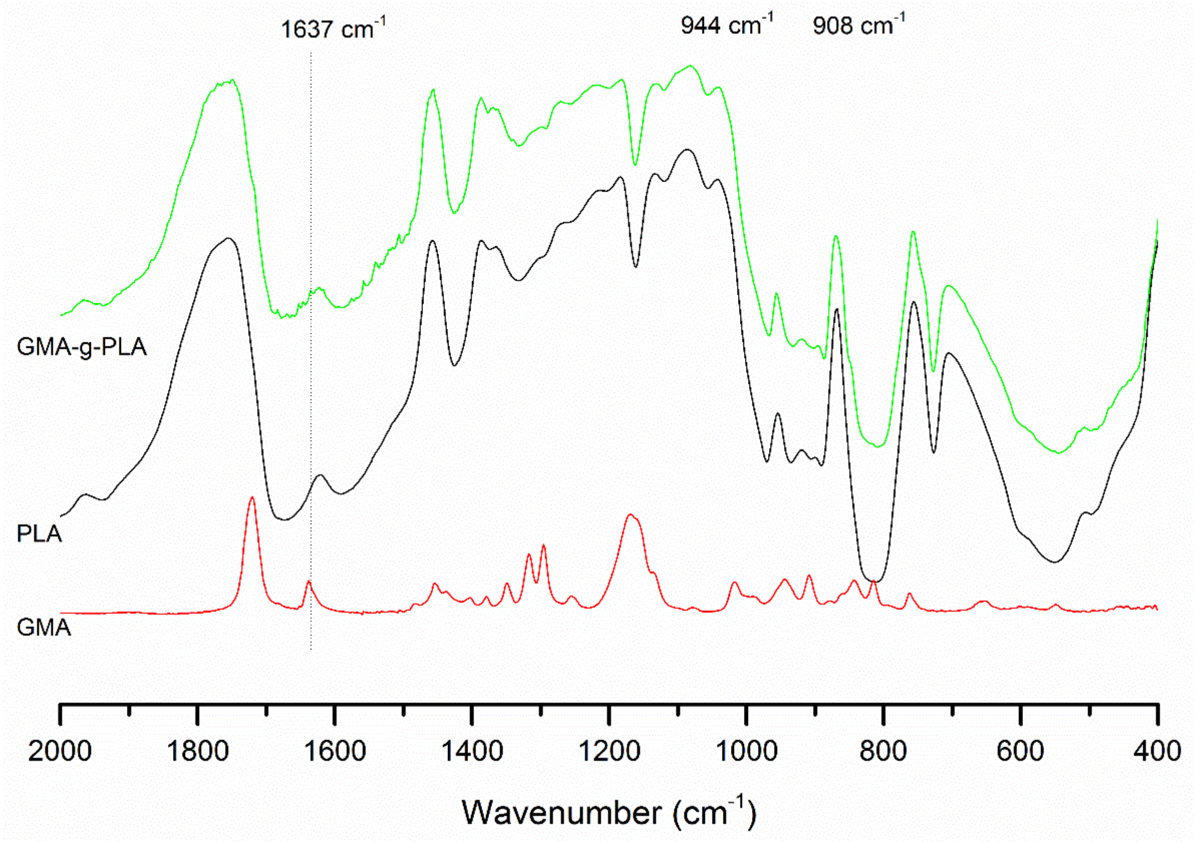


Figure 4 Infrared spectra of pure PLA, GMA, and graft copolymer prepared using TBPB.

The FTIR spectra of GMA-g-PLA (**Figure 4)** featured a peak at 908 cm^{-1}, which corresponds to the GMA, which was also noticeable in the pure GMA sample. This peak corresponds to the asymmetric stretching vibration of the epoxy group of GMA[43].

This FTIR peak further supported the grafting of the free radical of GMA on to the PLA polymer chain through the acrylic acid groups of GMA[34]. The GMA-g-PLA retained the epoxy groups of GMA. Overall, FTIR confirmed the formation of graft copolymer GMA-g-PLA containing epoxy groups.

3.2 Crystallinity Analysis

DSC curves of PLA and HH/PLA composites are presented in **Figure 5**. The corresponding thermal properties are summarized in **Table 2**. With the addition of HH, the cold crystallization peak shifted to a lower temperature as compared to the cold crystallization of neat PLA. The lower T_c observed in the heating run is attributed to accelerated crystallization induced by HH, which is known as a nucleating agent for PLA[48].

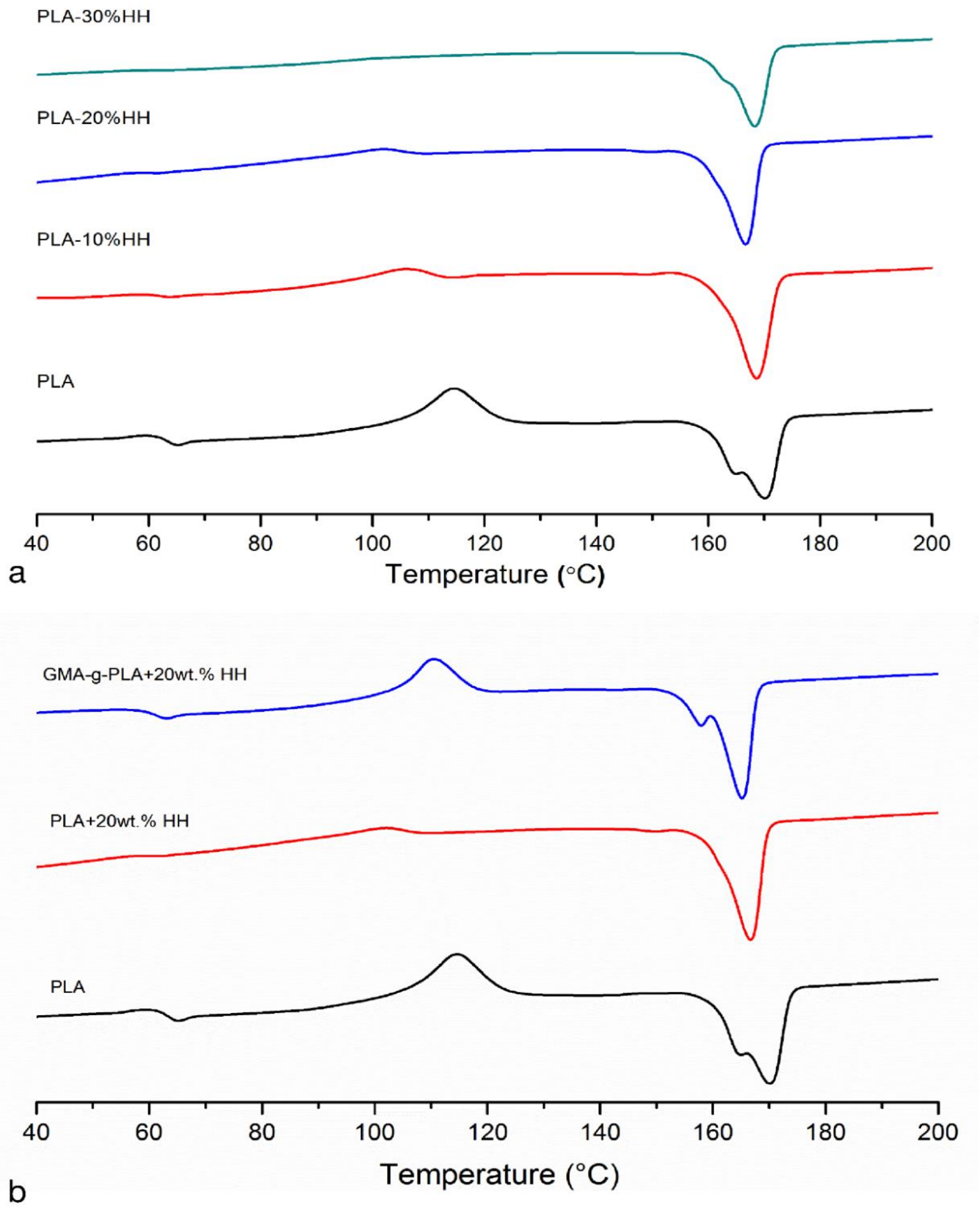


Figure 5 DSC curves of (a) PLA with increasing HH content, and (b) HH/PLA biocomposite with and without grafted GMA.

Figure 6 shows the proposed scheme of HH nucleation in PLA matrix. HH allows heterogeneous nucleation, which induces a decrease of the free energy barrier, and accelerates the crystallization. The endotherm peak (sharp endotherm peak at 164ºC with a shoulder peak at around 170ºC) corresponding to the fusion of the PLA crystallites (T_m) was identified at 170ºC for the biocomposite blends. This nucleation behavior during crystallization of PLA is an effect of the lamellar rearrangement of the polymer as well as the reorganization of less crystalline regions as crystalline structures within PLA[49].

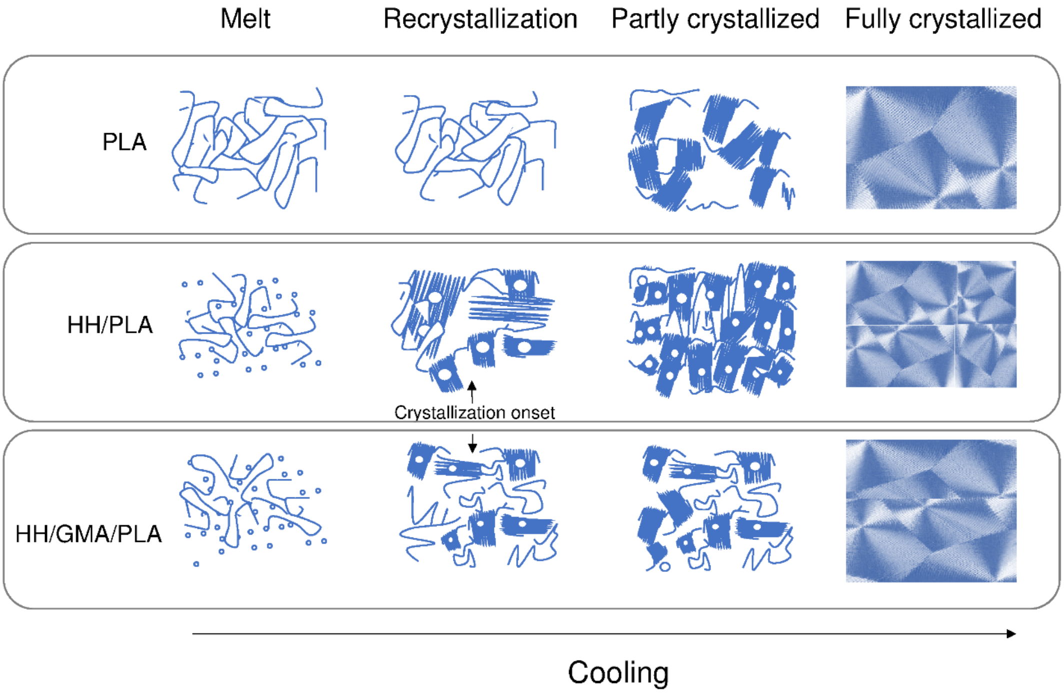


Figure 6 Schematic of the proposed route of nucleation of HH in the PLA matrix.

The degree of crystallinity (**Table 2**) of HH/PLA composites was higher than that of neat PLA. The increase of crystallinity confirmed the hypothesis of cellulosic fiber causing additional nucleation. However, a lower crystallinity yield was observed for the HH/GMA/PLA composites as compared to the HH/PLA. The grafting of amorphous GMA to the PLA causes an increase in the amorphous nature of the GMA-g-PLA in comparison to baseline PLA polymer. The increase in amorphous character of the GMA-g-PLA is however alleviated by the addition of HH, which increases the crystallinity of the GMA-g-PLA/HH biocomposites, albeit with crystals of lower quality and lower size, because of an overall faster rate of crystallization, as elucidated in **Figure 6.**

Table 2 Thermal Characteristics of PLA and HH/PLA Biocomposites

Composition	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_f (J/g)	X (%)
PLA	62.6	114.7	170.3	17.4	29.6	13.1
PLA/HH-10	61.5	106.0	168.0	4.4	31.7	32.6
PLA/HH-20	61.0	102.0	166.0	2.1	25.7	31.8
PLA/HH-30	58.6	104.0	168.0	0.2	22.6	34.5
GMA-g-PLA	64.0	117.0	165.0	0.5	27.3	29.2
PLA/GMA/HH-20	60.2	110.6	165.0	12.0	27.0	20.5

The thermal behaviors of the PLA/HH and GMA-g-PLA/HH biocomposites are consistent with the findings from the literature. The addition of wheat straw to PLA caused addition nucleation, and increased the degree of crystallinity[39] in the biocomposite, however, the degree of crystallinity decreased when GMA was added. This decrease in crystallinity is because of GMA grafting to the PLA polymer results in the increase of amorphous regions. In the HH/GMA/PLA composites, (a) the faster crystallization caused by the filler, and (b) the increased amorphous character caused by GMA grafting leads to an overall lower crystallinity. Moreover, through reactive compatibilization (by adding PLA, HH, GMA, and TBPB), the free radicals from the initiator (TBPB) cause degradation of the polymer matrix in the biocomposite, which may also lead to reduction in crystallinity[38].

The crystalline structure of the neat PLA, HH, and HH/PLA composites were further characterized by XRD, and the results are shown in **Figure 7**. The first high intensity peak is observed commonly at 2θ of 16.5° in the PLA, which is attributed to the PLA base[50]. HH exhibited diffraction peaks at 2θ = 15.8° and 22.3° corresponding to the cellulose I polymorph structure with peaks at 15.8° and 22.3° attributed to the crystallographic planes (110) and (002) crystallinity planes of cellulose I, respectively, with cellulose crystallinity index determined as 40%. In the HH/PLA biocomposite, peak associated to PLA was detected along with the peaks corresponding to HH at 15.8° and 22.3° convoluted along with the PLA base peak of 16.5°. The contribution of the cellulose crystalline structure in the HH/PLA biocomposite crystalline structure is discernible through the presence of peaks from the PLA crystal structure and the HH cellulose polymorph.

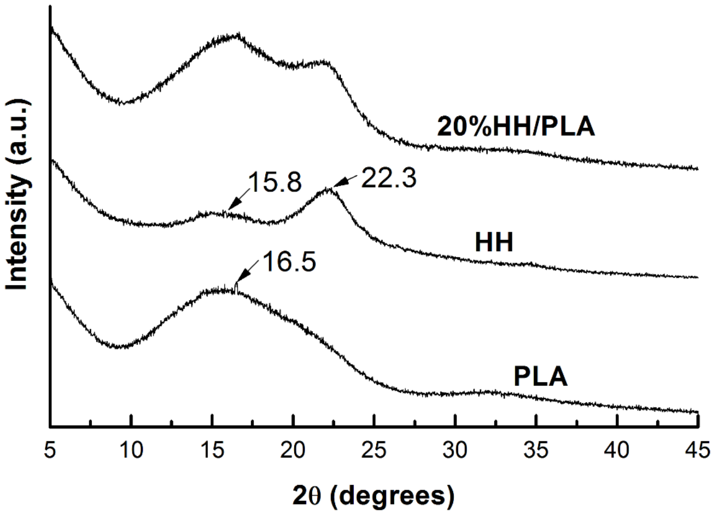


Figure 7 XRD patterns of PLA, HH and HH/PLA composites.

3.3 Thermomechanical Properties

TGA and DTGA curves of neat PLA, HH, and their composites are presented in **Figure 8**. In the case of HH, thermal degradation occurred in two stages. The initial 6 - 8% of weight loss is attributed to the residual moisture in the fiber[51]. However, after 250°C, the HH decomposes rapidly and the complete degradation occurs by 350 - 360°C. This second stage of degradation involves the degradation of hemicellulose, lignin, and cellulose[37]. These temperatures are in a similar range as analyzed by the U.S. Department of Agriculture[52] for wood, hemicellulose, cellulose, and lignin, inferred that hemicellulose is the least thermally stable compound, degrading around 300°C. Lignin degradation begins around 300°C, and finishes around 450°C. Cellulose degradation starts at 275°C, and is found to completely degrade at around 550°C[52]. Therefore, in all of the TGA curves of composites, two distinct degradation regions were observed. The first region is caused by the thermal degradation of cellulose, hemicellulose, and lignin in the HH[53], and the second higher temperature region is attributed to depolymerization of the PLA[54].

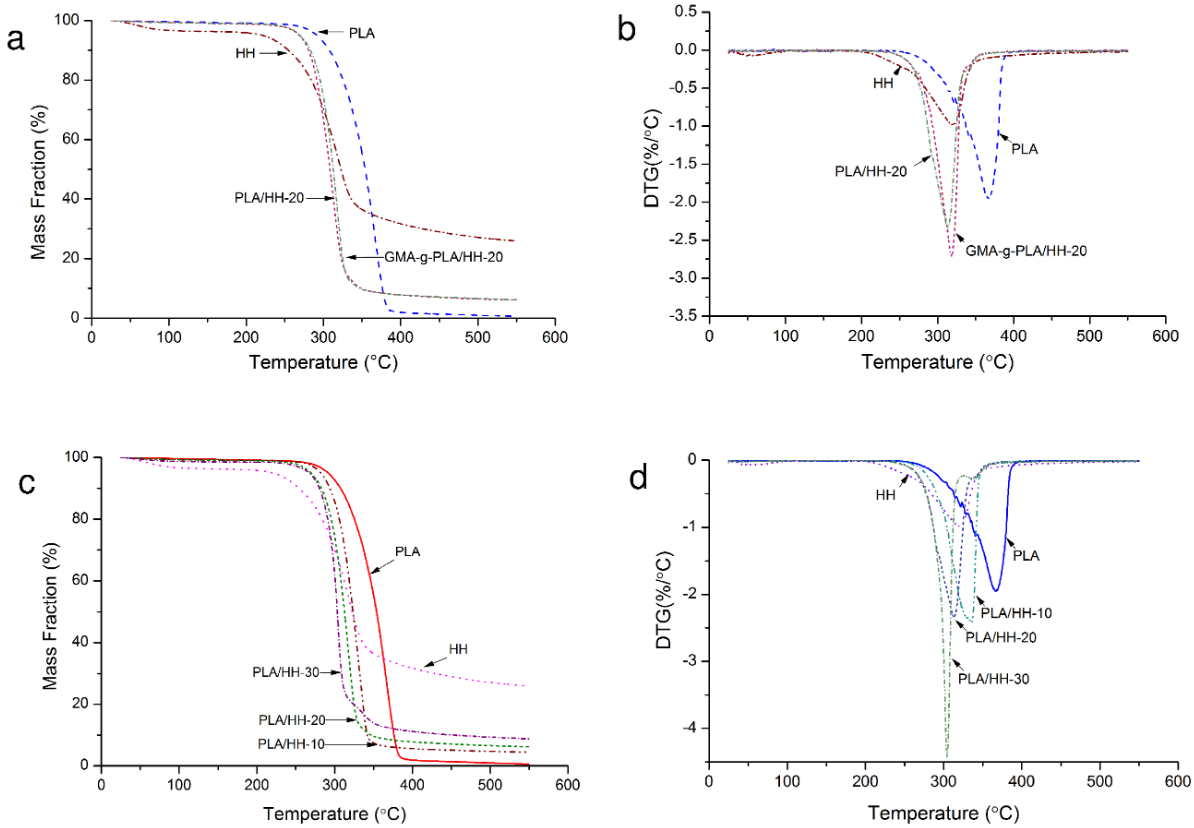


Figure 8 Thermal stability of the neat PLA and biocomposites shown as (a, c) TGA, and as (b,d) derivative TGA as a function of the filler content and GMA compatibilizer.

The characteristic thermal degradation parameters are listed in **Table 3**. For neat PLA and HH/PLA biocomposite, a single step decomposition process was observed from the derivative thermogram (DTG). Neat PLA showed an onset temperature at 291°C and the final decomposition temperature at 367°C, with a residual mass fraction of 0.6% at 550°C. The onset of thermal decomposition of HH/PLA composites is lower than neat PLA, indicating the introduction of HH decreases the thermal stability because of low degradation threshold temperatures of lignocellulosic constituents present in HH. The final decomposition temperature of GMA-g-PLA/HH biocomposite increased in comparison to the biocomposite without GMA compatibilization. Through GMA-assisted compatibilization, enhancement in interfacial adhesion and hence an improvement in temperature of thermal degradation initiation is observed.

Table 3 Thermal Stability Characteristics Determined from TGA

Specimen	T_5 (°C)	T_{50} (°C)	$T_{\max}$ (°C)	Residue (%) at 550°C
PLA	291	354	367	0.6
HH	221	322	322	25.9
PLA/HH-20	269	308	312	6.1
PLA/GMA/HH-20	269	312	318	6.2

3.4 Fractography Analysis

SEM micrographs (**Figure 9)** show the comparison of the fracture surfaces of HH/PLA and HH/GMA-g-PLA biocomposites, specifically the interfacial behavior upon fracture. Voids, fiber fracture, and pullout (shown with arrows) were observed in the uncompatibilized biocomposite **(Fig 9 a-b)**, and these artifacts were attributed to the absence of effective interfacial adhesion, and thereby a plausible reduction in tensile, flexural, and impact strength. However, lesser and shorter fiber pullouts were observed when the composites were compatibilized with GMA **(Fig 9 c-d)**, which also appear to be coated with PLA. These observations suggest effective adhesion between the HH and PLA matrix in the composites with the GMA.

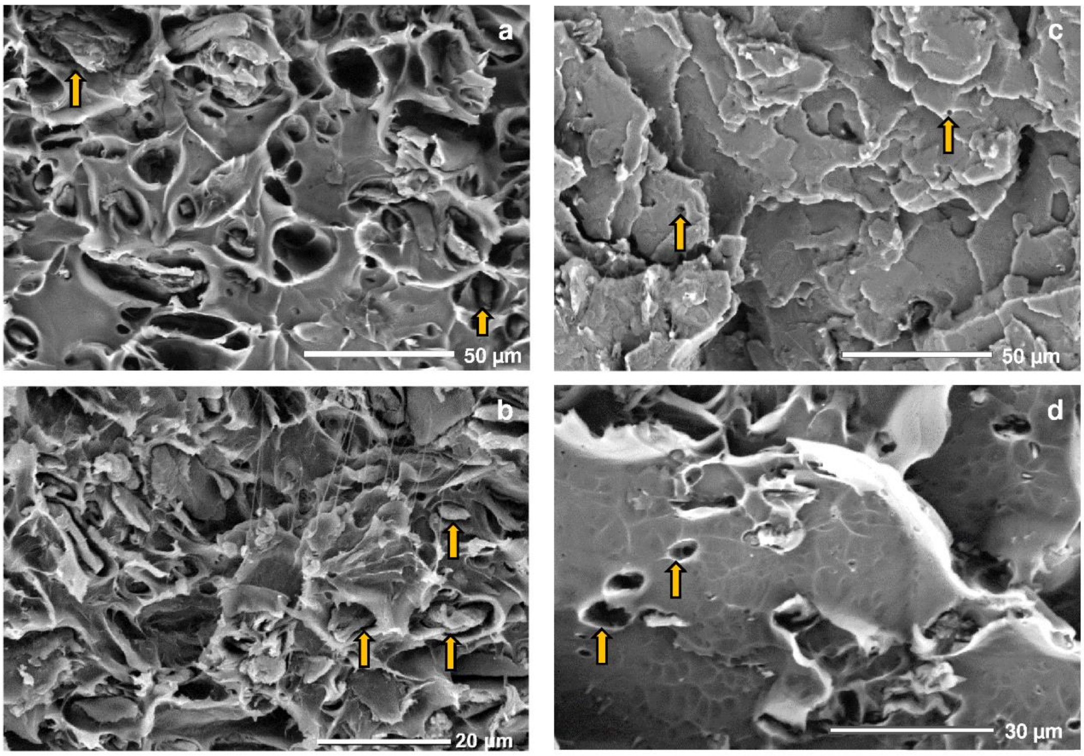


Figure 9 SEM images of flexural fracture surface of PLA/HH-20 (a, b) and GMA-g-PLA/HH-20 (c, d) biocomposites, showing key characteristics of the fracture surfaces.

3.5 Mechanical Property Analysis

3.5.1 Tensile Properties

The average tensile strength and Young's modulus of the HH/PLA composites are shown in **Figure 10**. The elastic modulus increased with an increase in HH weight fraction in the biocomposites, while tensile strength decreased concurrently. The reduction in strength in the composites is attributed to an embrittlement caused by the filler acting as discontinuities that restrict polymer chain movement, and hence a lower elongation is observed upon a mechanical energy input[55]. Furthermore, inadequate fiber wetting also leads to an incompatible fiber-matrix interface. Such flaws and imperfections can induce fracture in semi-crystalline polymers[56]. Compared to continuous fibers, HH lacks sufficient length to trigger toughening mechanisms that impede brittle fracture[14].

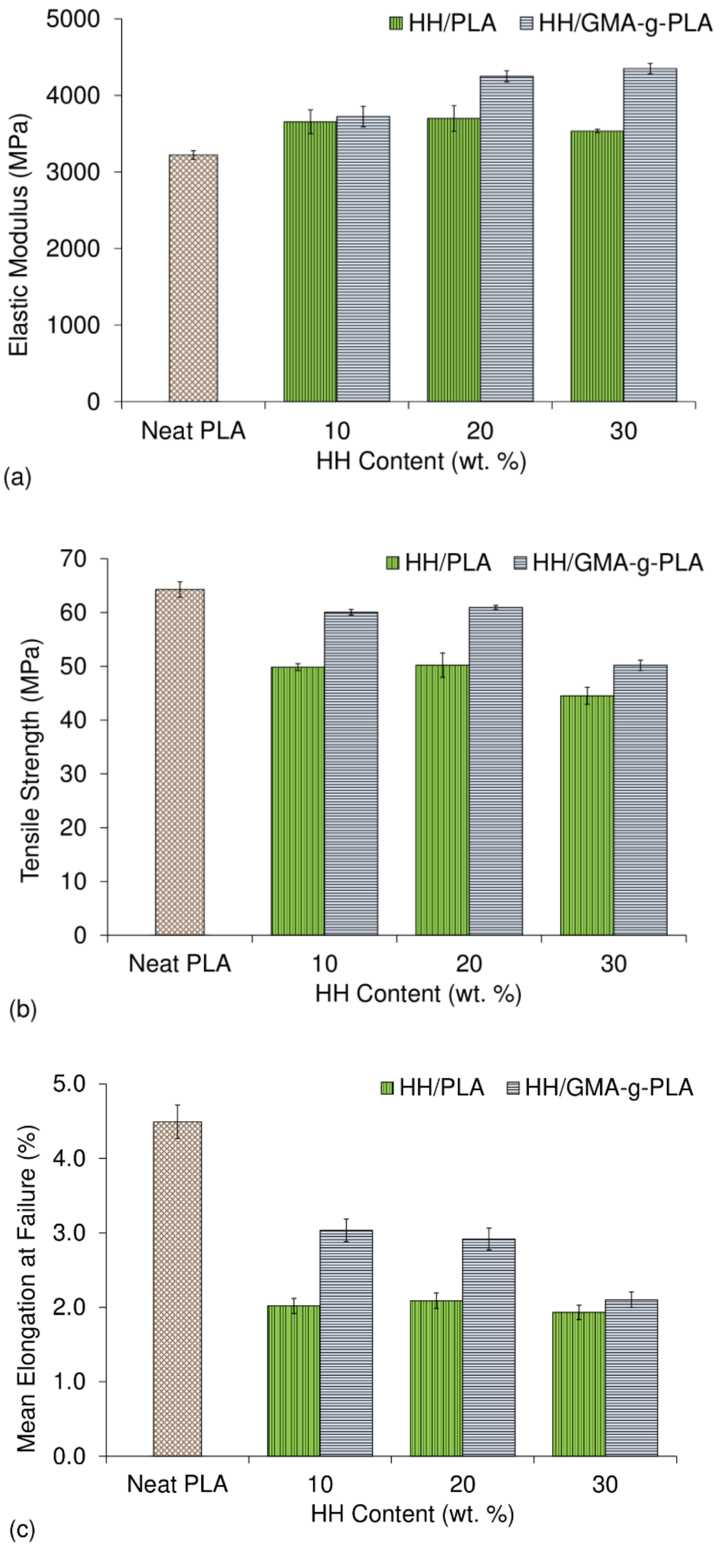


Figure 10 Tensile (a) modulus, (b) strength, and (c) elongation to failure of PLA/HH and GMA-g-PLA/HH biocomposite as a function of HH content, compared to neat PLA.

However, the tensile strength was significantly improved in comparison to the non-compatibilized biocomposite when GMA was grafted to modify the PLA. Without GMA grafting, the tensile strength reduced from 65 MPa to 50 MPa with 10 wt. % and 20 wt. % of HH addition with a retention of 77% compared to neat PLA. However, with 1 wt. % GMA grafting, the tensile strength improved to 61 MPa, at a retention rate of 94% compared to neat PLA. GMA grafting clearly enhanced the interfacial adhesion between PLA and HH.

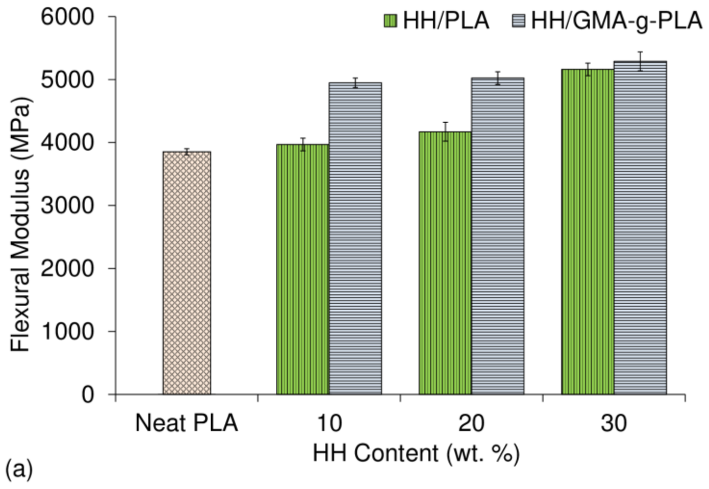
Nevertheless, the addition of more than 20% HH caused a decrease in tensile strength. Crystallization of the PLA matrix enhanced stiffness and brittleness of the neat PLA and composites, which was reflected in increased modulus and in diminished strength respectively. However, GMA improved the interfacial adhesion and contributed for higher strength of composites. HH inclusion exhibited a stronger effect on the modulus in the PLA matrix. This increase is because of the nucleation capability of HH in PLA crystallization[57], as also evidenced by DSC measurements (**Figure 5**).

The increase in tensile strength is consistent with the tensile behavior of PLA reinforced with particulate fillers, and compatibilized through the addition of GMA as an interfacial agent. The tensile strength of PLA reinforced with particulate fillers such as bamboo flour, wheat straw, and rice husk with GMA[40,41] or maleic anhydride[39,46,58] showed increases in tensile strength at concentrations of 2 – 5 wt % of the compatibilizer. The tensile strength of the compatibilized biocomposites in most cases is greater than the non-compatibilized biocomposites, and comparable with the neat PLA.

The tensile (elastic) modulus of thermoplastic biocomposites filled with particulate fillers increases with the increase in the elastic filler content to a critical maximum, but with a concomitant decrease in the ductility of the biocomposite[59–61]. In PLA/particulate filler biocomposite blends, the tensile modulus shows increases with the addition of an interfacial compatibilizer such as GMA[40,41] or maleic anhydride[39,58].

3.5.2 Flexural Properties

The average flexural strength and flexural modulus of the HH/PLA composites as a function of fiber content are presented in **Figure 11**. The flexural strength decreased with increased fiber content. For instance, flexural strength of PLA was decreased from 103 MPa to 82 MPa with a 10 wt. % of HH. This decrease is attributed to the inability of the HH with irregularly shaped particles to support stresses transferred from the PLA matrix and inadequate interfacial bonding, which is the resultant of voids created at the HH/PLA interface, and causing a weak structure[62].



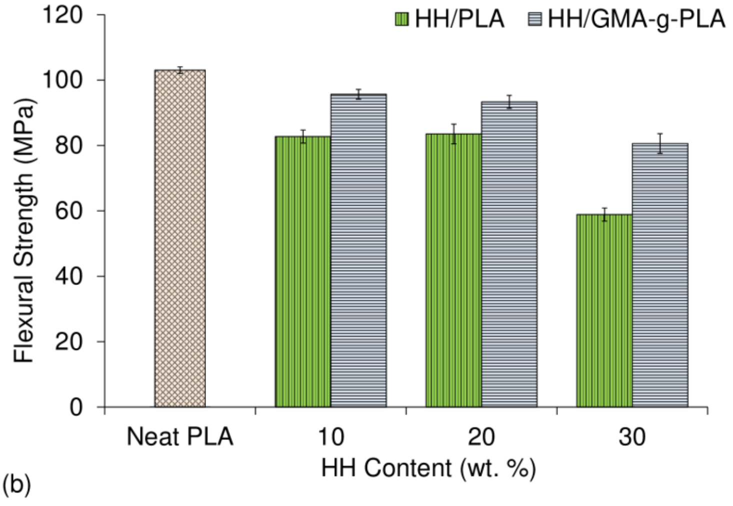


Figure 11 Flexural (a) modulus, and (b) strength of PLA/HH and GMA-g-PLA/HH biocomposites as a function of HH content, in comparison to neat PLA.

In contrast to flexural strength, **Figure 11b** shows that flexural modulus of the composites increased as the fiber content increased. With the addition of 20 wt. % HH, the flexural modulus of PLA was increased from 3.8 GPa to 4.1 GPa. The inclusion of HH (elastic particulate) to a (plastic) PLA[63] causes restricts chain movement and hence shows a higher stiffness in comparison to the neat polymer, which can show a relatively higher deformation at an equivalent stress. The flexural modulus for a PLA/wheat straw biocomposite[39] showed marginal variation with the addition of the interfacial compatibilizer in comparison to the non-compatibilized grade, and an average of 64% increase over the neat PLA.

As shown in **Figure 11**, GMA grafting in the compatibilized biocomposites caused an increase in the flexural strength and flexural modulus of the composites. The higher flexural strength and flexural modulus of the biocomposite with GMA compatibilization compared to the biocomposite without GMA is attributed to the increase in interfacial adhesion between HH and PLA as reported previously[41]. The PLA/GMA/HH biocomposite with 10 wt. % HH showed the highest flexural strength of 95.6 MPa. Similarly, the flexural strength showed increases with the addition of 3 – 5 phr of maleic anhydride grafted PLA over the non-compatibilized biocomposite[39], and was comparable with the neat PLA flexural strength.

3.5.3 Notched Impact Properties

The average notched impact strength of the HH/PLA composites is shown in **Figure 12**. The notched impact strength decreased with increasing HH content. The impact strength of PLA decreased from 2.99 kJ/m^2 to 2.57 kJ/m^2, when filled with 10 wt. % HH. The reduction in impact strength of PLA by incorporation of natural fibers is consistent with existing literature[64]. This decrease is because of insufficient adhesion between PLA matrix and HH, which cause the fibers to become sites of stress concentration, inducing micro-voids between the HH and PLA matrix. The micro-cracks arising from the micro-voids upon impact energy incidence induce crack propagation easily, and therefore decrease the impact strength of the biocomposites.

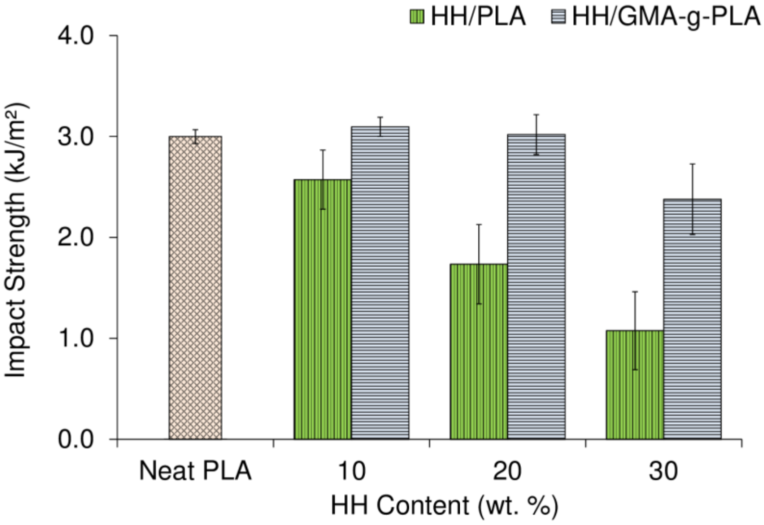


Figure 12 Impact strength of the HH/PLA and GMA-g-PLA/HH biocomposites in comparison with neat PLA and increasing HH content.

The impact strength of the HH/PLA biocomposite increased upon the use of GMA as a compatibilizer. With the addition of GMA at the 10 wt. % HH, the average impact strength 3.1 kJ/m^2 was attained, higher than neat PLA (2.99 kJ/m^2). The impact strength data demonstrated that the addition of GMA possesses the potential of improving physical and mechanical properties of HH/PLA composites. These results are consistent with the SEM fractography analysis shown in **Figure 9**. The impact strength was increased by 10% in a PLA filled with 30 wt. % wheat straw upon the addition of 5 phr of PLA-g-MA[39]. Similarly, with the addition of 10 phr and 15 phr PLA-g-GMA, the greatest impact strengths of 14.5 kJ/m^2 and 14.4 kJ/m^2, respectively, were observed in PLA/bamboo flour biocomposites[40].

Overall, the inclusion of HH alone to the PLA caused an increase in the elastic/flexural modulus and a decrease in strength of the HH/PLA biocomposite in comparison to the neat polymer. The grafting of GMA to the HH/PLA system caused increases in the interfacial compatibility and thereby the strength of the biocomposite blends. Hence, the addition of GMA was deemed highly beneficial for achieving a balance of mechanical and thermo-physical properties.

4 Conclusions

Broader public consciousness on climate change and resource depletion is causing an increasing demand for sustainable products based on renewable resources. In this study, biomass waste HH was investigated as a filler to reduce the cost of PLA while preserving the biodegradability, with GMA as an interfacial compatibilizer. With GMA grafting, the HH/PLA retained a major fraction of the PLA mechanical properties at 10 wt. % and 20 wt. % HH inclusions. Effective interfacial adhesion between the PLA and HH in the composites compatibilized with GMA was confirmed through SEM analysis. An increase of crystallinity of PLA in composites determined through DSC and XRD, confirmed the role of HH as a nucleating agent. The onset of thermal decomposition of the biocomposites obtained through TGA was marginally lower than that of neat PLA. Largely, the effect of GMA on the mechanical properties and interfacial adhesion of the HH/PLA bio-composites was advantageous. The HH/GMA-g-PLA possesses the potential to be cost-competitive, and be durable in service and biodegradable post-service, hence valuable for packaging and disposable goods applications that require dimensional and thermal stability.

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4.3 Paper-V: Processing and Properties of Antibacterial Silver Nanoparticle-loaded Hemp Hurd/Poly(lactic Acid) Biocomposites

Khan, B. A, Chevali, V. S., Na, H., Zhu, J., Warner, P and Wang, H. (2015). Processing and Properties of Antibacterial Silver Nanoparticle-loaded Hemp Hurd/Poly(lactic Acid) Biocomposites. Composites Part B: Engineering, Vol. 100, pp 10-18

The inherent antibacterial property of hemp hurd was further enhanced using silver nanoparticle loading. The objective of this article was to produce an effective antibacterial biocomposite using poly(lactic acid) as matrix, silver nanoparticles loaded hemp hurd as antibacterial biobased filler and glycidyl methacrylate as compatibilizer. The characterization results of the developed biocomposites were promising. The overall contribution of this article in this thesis is to provide understanding on the discernible potential of the developed antibacterial biocomposites for food packaging application.

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Processing and properties of antibacterial silver nanoparticle-loaded hemp hurd/poly(lactic acid) biocomposites

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ABSTRACT

The use of silver nanoparticles in providing effective antibacterial resistance in glycidyl methacrylate-compatibilized hemp hurd-filled poly(lactic acid) biocomposite is presented. The thermal and mechanical properties, and antibacterial resistance against gram negative *E. Coli* was investigated, and characterized using X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, and scanning electron microscopy. The inclusion of glycidyl methacrylate assisted in elastic moduli and strength increases at 10–30 wt % fraction of silver nanoparticle-loaded hemp hurd in poly(lactic acid), with 20 wt % hemp hurd-filled biocomposite exhibiting the highest range of properties within the biocomposites investigated. The inherent antibacterial property of hemp hurd was further enhanced using silver nanoparticle loading to achieve a safe level of heavy metal migration at 0.20–3.08 mg/kg. Effective antibacterial activity was achieved with distinct decreases of 85% and 89% in bacterial growth at 0.025 wt % and 0.05 wt % loading of silver nanoparticle in the biocomposite. Overall, the properties of these novel biocomposites demonstrated discernible potential in further development of food packaging applications.

1. Introduction

Biodegradable food packaging comprises the largest market for biodegradable plastics [1] with a 65% market share, driving innovation in biodegradable polymers and their biocomposites. Specifically, biodegradation in landfill or composting without toxic emissions [2] is constantly strengthening their demand and growth. Poly(lactic acid) (PLA) and poly(hydroxy alkanoates) (PHA) are at the forefront of academic and industry biopolymer research, often combined with microscale and nanoscale plant-based filler inclusions to achieve sustainability and multifunctionality [3–9]. PLA specifically is unarguably the foremost candidate for replacing conventional petrochemical based thermoplastics, offering desirable mechanical properties and versatility in processing [3,10–12]. Nonetheless, antibacterial property is a major consideration for selection of bioplastics for semi-rigid food packaging applications in addition to thermal/dimensional stability.

Antibacterial agents are often compounded for this reason with PLA to achieve an antibacterial action [13–17]. The most common antibiotic chemicals used today are triclosan, biocides (e.g., *N*-(trichloromethylthio)phthalimide, 3-Iodoprop-2-yn-1-yl butylcarbamate), nanoparticles, quaternary salts, and heavy metals (e.g., silver (Ag), mercury (Hg), tellurium (Te)) [18,19]. Heavy metals act as antibiotic agents [18] through (a) causing protein dysfunction, (b) depleting antioxidants through production of oxygen species, (c) impairing function of the membrane, (d) disrupting assimilation of nutrients, and (e) damaging genetic code through cell mutation. Heavy metals in low loadings, particularly at nanoscale are extremely effective for plastic packaging. Nevertheless, a heavy metal such as silver is often seen as harmful for all living cells, and hence viewed as a toxic substance, whose usage and release from plastics in the nanoparticle form is a subject of investigation in the scientific community. Authorities throughout the world, of which the European Union Directive 2002/72/EC is well established and heeded, govern the migration and release rates of silver nanoparticles (AgNP) into food and water. The ultimate goal of scientific studies today is to minimize the migration rate of AgNPs into food/food simulants and thereby to minimize the toxicity potential for human physiology, yet maintaining an antibacterial resistance.

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Lignocellulosic materials obtained from flax (*Linum usitatissimum* L.) and hemp (*Cannabis sativa* L.) plants address the objective of achieving antibacterial activity and minimizing heavy metal migration. Plant based resources such as flax and hemp containing considerable fraction of lignin, which binds heavy metals through adsorption or absorption [20]. However, this absorption potential differs within various portions of the plant, and understandably, a porous structure with a larger surface area can be surmised to possess a strong capability for diffusion and adsorption of heavy metal ions.

The critical analysis of the multifunctionality of such a porous structure, i.e., hemp hurd (HH), is the objective of the current study. The hemp hurd as shown in Fig. 1 is the residue obtained after the extraction of bast fibers and other commercial bio-products of the industrial hemp plant, and is obtained in an aspect ratio analogous to a filler, with average particle size of about 40 μm (Fig. 1b). As seen in Fig. 1a, the hemp hurd constitutes a 70–80% of the hemp stem, and is characterized by a porous structure as seen in the transverse cross section (Fig. 1c) and the longitudinal cross section (Fig. 1d). HH is gaining prominence as a bio-based filler, however a majority of HH is mostly disposed by combustion or landfilling causing environmental pollution, albeit a limited volume of HH is also used for animal bedding and for construction materials [21,22]. Novel pathways for adopting HH are under development, e.g., ethanol production [23], with success dependent on achieving a high yield per kg. HH, however, bears substantial potential for compounding with PLA as a biocomposite for food packaging applications. A previous study by the authors indicated that HH exhibits antibacterial activity against *Escherichia coli* (*E. coli*) [24]. However, the performance of HH as a constituent in PLA-based biocomposites is relatively unknown, and often overshadowed by hemp, sisal, jute and kenaf bast fibers, whose utilization has increased in the recent past [25], reaching pilot/commercial scales. The introduction of HH into biocomposite blends is only effective if the interfacial incompatibility between the filler and the thermoplastic polymer can be engineered to achieve adequate physical and mechanical stability [26]. The surface modification of plant based fillers is imperative with surface compatibilizers such as isocyanates and maleated compounds are widely used for this purpose [27–29]. Glycidyl methacrylate (GMA) is emerging as a compatibilizer for PLA and other thermoplastics [30–32], with demonstrated increases in mechanical properties realized in high density polyethylene/rice-husk [33] and PLA/bamboo flour biocomposites [34,35] with GMA compatibilization.

A majority of published research in hemp/PLA (as bast fiber or hurd) focuses on improvements in mechanical, thermal and interfacial properties [11,28,36–41].

To the knowledge of authors, there is no existing comprehensive research on the antibacterial performance of HH-reinforced PLA biocomposite. The objectives of the current study are two fold, i.e., (a) assess the multifunctionality of HH as an antibacterial agent in the biocomposite form in addition as a structural filler, and (b) assess the role of HH as a carrier for an external antibacterial agent, i.e., AgNPs. The ultimate goal of this study is to develop a multifunctional biocomposite with PLA, HH, and AgNPs that exhibits a mechanical, thermal, and antibacterial performance that exceeds the effectiveness of the base PLA for food packaging applications at a lower overall cost.

Three main extruded, injection molded materials were produced and investigated for this study, i.e., (a) neat PLA, (b) PLA with 10–30 wt % AgNP-loaded HH filler, and (c) GMA-grafted PLA with 10–30 wt % AgNP-loaded HH filler. In addition to mechanical, chemical, and thermal characterization, the antibacterial properties were also investigated against bacteria *E. coli*. Silver migration from the AgNP-HH/PLA and AgNP-HH/GMA/PLA biocomposites was analyzed using industry standards for packaging.

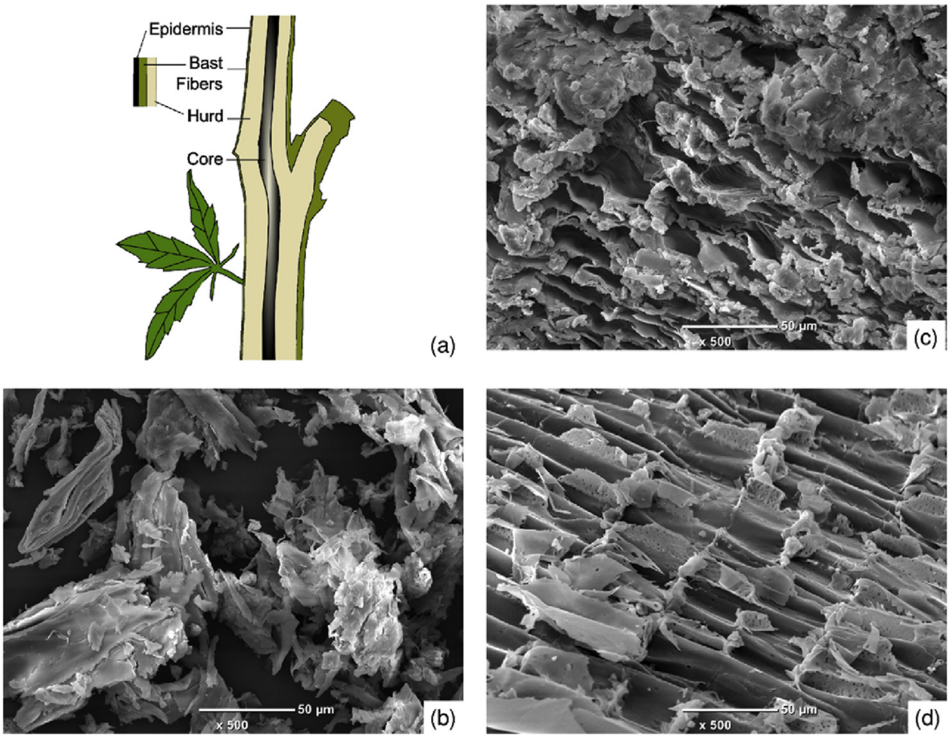

Fig. 1. The morphology of hemp plant and the derivative hemp hurd shown as (a) component of the stem, (b) pulverized as filler, (c) transverse hurd cross section, and (d) longitudinal hurd cross section.

2. Processing and experimental methods

2.1. Materials and biocomposite processing

Commercial PLA (Grade 4032D, $\rho = 1.24$ g/cm^3, $T_m = 155°C–170°C$) was purchased from Nature Works, LLC. (Minnetonka, MN). Hemp hurd powder with a mean particle size of 40 μm was obtained from Ecofibre Industries Operations Pty Ltd, Australia. glycidyl methacrylate (GMA) and tert butyl perbenzoate (TBPB) were supplied by the Ningbo Institute of Industrial Technology, and were used with no further purification. The silver-based antibacterial agent was synthesized in-house, and precipitated on the HH filler using a proprietary method developed in collaboration with Ecofibre Industries Pty Ltd.

The HH, AgNP-HH and PLA were vacuum-dried at 80°C for 24 h. Neat PLA, HH/PLA, HH/GMA/PLA, AgNP-HH/GMA/PLA, and AgNP-HH/PLA and were melt-blended using a laboratory-scale conical twin screw extruder (Ruiming Plastics Machinery, Wuhan, China) with rotational speed of 40 rpm at 175°C for 10 min. All materials were subsequently injection molded into standard test bars via a miniature injection machine (SZ-15, Wuhan, China). The injection pressure, temperature, and time were set as 3 MPa, 200°C and 30 s, respectively, with the mold temperature maintained at 40°C.

2.2. Biocomposite characterization and properties testing

Wide-angle X-ray diffraction (WAXD) analysis was performed on a D8 Advance diffractometer (Bruker AXS) with a Cu K_α radiation (λ_x= 0.154 nm). The equipment was operated at 40 kV and 40 mA at ambient temperature. The scan range was between $2\theta = 5°–40°$ with a scan speed of 3.5°/min.

The morphology of the blends was imaged by a scanning electron microscope (SEM, Hitachi TM-1000) at an accelerating voltage of 10 kV. The fractured (in liquid nitrogen) surfaces were sputtered with gold prior to examination.

The thermal properties of the biocomposites were characterized using differential scanning calorimetry (DSC) on a Mettler Toledo TGA/DSC1 analyzer (Mettler-Toledo, Switzerland). The samples were stabilized at 30°C for 1 min before they were heated to 200°C at 10ºC/min, and maintained at 200°C for 3 min to erase thermal history, prior to cooling down to 30°C at 25ºC/min. After 1 min at 30°C, a second scan from 30°C to 200°C at 10ºC/min was performed. Throughout the whole process, the sample cell was kept under a nitrogen flow of 20 mL/min. The glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) were determined from the second scan. T_m and T_c were taken as peak values, and T_g was taken as the midpoint of heat capacity changes. When multiple endothermic peaks were obtained, the peak temperature of the main endotherm was recorded as T_m. The crystallinity percentage (X) of PLA and the biocomposites was calculated by using Equation (1).

$$X = \left(\Delta H_f - \Delta H_{cc}\right) \Big/ \left(\Delta H_f^0 w\right) \tag{1}$$

where $\Delta H_f^0 = 93$ J/g for 100% crystalline PLA [42], ΔH_f is the enthalpy of melting, ΔH_{cc} is the cold crystallization enthalpy, and w is the weight fraction of PLA in the biocomposite.

Thermogravimetric analysis (TGA) was used to evaluate the thermal stability on a Mettler Toledo TGA/DSC1 analyzer at a linear heating rate of 10 °C/min under a nitrogen atmosphere. The temperature range was 25°C–550°C, with the mass of samples kept at 3 mg–5 mg. Differential TG curves (DTGA) were obtained from the first derivative of the TGA data.

An Instron 5567 was used for the mechanical property measurements according to the GB/T 1040.1–2006 standard. The standard bar-shaped samples were used to determine the tensile strength (TS), tensile modulus, (E) and elongation at break (EB) on five specimens for each biocomposite were tested at a crosshead speed of 20 mm/min.

2.3. Antibacterial testing

The biocomposite antibacterial performance were tested on *E. coli* (ATCC # 25922), which is a common bacterial strain used for antibiotic testing. The bacterial cultures were maintained on nutrient agar slopes. They were grown in a sterile tryptic soy broth, and incubated at 37°C for 24 h. The working buffer solution (0.3 mM KH_2PO_4) was adjusted to a pH of 7.2 ± 0.1 with a diluted solution of NaOH, and then capped, sterilized, and stored at room temperature.

The working bacterial solution was prepared using the aforementioned culture, which was diluted using a sterile buffer solution until the solution attained an absorbance of 0.28 ± 0.02 at 475 nm measured spectrophotometrically, which corresponds to a concentration of $1.5 \times 10^8–3.0 \times 10^8$ colony forming units per milliliter (CFU/mL). An Atherton Cyber series autoclave was used for sterilization and media preparation at 121°C for 20 min. Antibacterial performance of the hemp hurd powder was investigated according to ASTM E2149-10 standard.

2.4. Silver concentration and migration testing

The European Council Directive 82/711/EEC dictates the migration testing of the constituents of plastic materials and articles that may contact with food, and the list of food simulants used for such testing. In this study, Ag migration from the AgNP-HH/PLA is measured according to Council Directive 82/711/EEC published by European Commission in 1982. 3% (v/v) aqueous acetic acid and 95% (v/v) aqueous ethanol were selected as food simulants, which simulates all alcoholic, aqueous, and acidic foods, albeit at a higher concentration of the alcohol, which is specified at 10% (v/v) in the standard.

Analytical portions (0.1 g) of biocomposites were weighed into each PTFE vessel, and 6 mL of HNO_3 and 2 mL of H_2SO_4 were added. The samples were digested using a microwave oven. The digested solution was diluted with Milli-Q water to 50 mL and analyzed with an Elmer Optima 2100 DV ICP-OES with radio frequency power of 1450 W, plasma gas flow of 15 L/min, auxiliary gas flow of 0.2 L/min, nebulizer gas flow rate of 0.8 L/min, and sample flow rate of 1.5 mL/min.

To determine the chemical element migration behavior of the biocomposites in the stated food simulants, biocomposites samples (0.15 g) were placed in 50 mL glass vials, and 30 mL of 3% (v/v) aqueous acetic acid or 95% (v/v) aqueous ethanol were added to the vials and sealed. The samples were left for specific time intervals (10 h) at specific temperatures (40°C, 70°C) in an oven. The amount of Ag in the two food simulants at each temperature–time condition was determined. After removal of the biocomposite strip, the migrated simulant was evaporated to dryness in the water bath kettle. The concentration of Ag was measured at specific wavelength (328.068 nm) using an inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 2100 DV).

3. Results and discussion

3.1. Silver binding characterization

The XRD patterns of HH, AgNP-HH, and AgNP-HH/PLA biocomposites are shown in Fig. 2a. The untreated HH showed

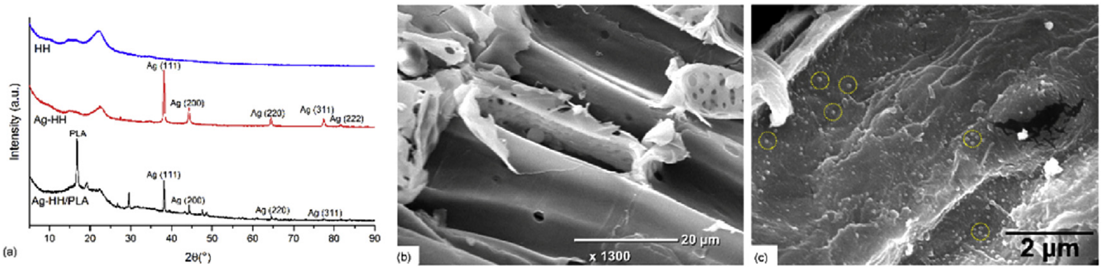

Fig. 2. The characteristic (a) XRD patterns of HH, AgNP-HH and AgNP-HH/PLA biocomposites, (b) pristine hemp hurd surface, and (c) SEM image of AgNPs loaded to HH.

diffraction peaks at $2\theta = 15.8°$ and 22.3°, corresponding to the (110) and (002) crystallographic planes of cellulose I respectively. The XRD spectra of AgNP-HH showed the crystalline peaks of silver in addition to the cellulose I peaks at 2θ values of 38.2°, 44.3°, 64.5°, 77.5° and 81.7°, corresponding to (111), (200), (220), (311) and (222) crystallographic planes of face-centered cubic (FCC) silver respectively [43]. The XRD spectra indicated the presence of Ag in HH. In the biocomposite form, the typical PLA peak at $2\theta = 16.5°$ was strongly visible in the biocomposite [44]. The HH peak and Ag peaks are also visible, although the a lower relative intensity of Ag peaks, as the total Ag content in the biocomposite is less than 0.05 wt % in the biocomposite. Furthermore, the binding of AgNPs on the HH was confirmed through SEM imaging as shown in Fig. 2c, which showed the presence of AgNPs as precipitated on the HH particulate. As shown, the near spherical AgNPs show a size of (75 ± 21) nm in diameter. The difference in surface appearance and the absence of precipitated nanoparticles is discernible against the untreated HH surface as shown in Fig. 2b.

3.2. Thermal properties

The DSC curves of PLA, AgNP-HH/PLA (20/80 wt %) and AgNP-HH/GMA/PLA (20/2/78 wt %) biocomposites are shown in Fig. 3a. The corresponding thermal properties obtained from the DSC data are shown in Table 1. Upon addition of AgNP-HH, the cold crystallization peak of the biocomposite shifted to a lower temperature as compared to the neat PLA. The lower T_c is indicative of accelerated crystallization induced by HH, which acts as nucleating agents for PLA [45]. HH hence allowed heterogeneous nucleation, decreasing the free energy barrier and hence accelerating the crystallization. The endothermic peak with a sharp endotherm peak at 164°C and a shoulder peak at around 170°C corresponds to the fusion of the PLA crystallites (T_m), and can be identified at 170°C for the samples. This phenomenon of PLA was reported to be an effect of lamellar rearrangement during crystallization of the polymer as well as the reorganization of regions of low crystallinity to form diverse crystalline structures in PLA [46]. The melting temperature is closely dependent on the size and the degree of crystallization of the lamellae [47]. Hence, the crystalline structure of the recrystallized materials can be conjectured to be near similar, as there is only marginal variation in the crystallinity values. AgNP-HH/PLA biocomposites showed a higher degree of crystallinity in comparison to neat PLA. This increase of crystallinity reinforced the presumption that lignocellulosic fibers cause nucleation [45]. Compared with AgNP-HH/GMA/PLA biocomposite, AgNP-HH/PLA biocomposite showed a higher crystallinity value. The compatibilization and resultant stronger adhesion between the PLA matrix and the HH because of GMA-g-PLA can be viewed as a cause for reorganization and potentially the specific crystallization of PLA. A lower crystallinity and a higher cold crystallization temperature of the AgNP-HH/GMA/PLA biocomposite was an effect of decrease in chain mobility. Hence, the inclusion of HH and GMA affected the crystallinity and crystallization of the biocomposite blends.

Table 1
Thermal characteristics of PLA and HH/PLA composites.

Composition	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_f (J/g)	X_{DSC} (%)
PLA	62.6	114.7	170.3	17.4	29.6	13.1
AgNP-HH/PLA	61.0	102.0	166.0	2.1	25.7	31.8
AgNP-HH/GMA/PLA	60.2	110.6	165.0	12.0	27.0	20.5

The TGA curves of pure PLA, AgNP-HH, and their biocomposites (containing 20% AgNP-HH) are presented in Fig. 3b. The melt recrystallization curves were obtained at 10°C/min in the range 25–550°C. In AgNP-HH, thermal degradation occurs in two stages, with the initial 6–8% of weight loss attributed to the loss of inherent moisture in the fiber. Beyond 250°C, HH decomposed rapidly and majority of decomposition is completed by 350–360°C. This second stage involved the degradation of hemicellulose, lignin and cellulose [28]. The constituents of the hemp hurd decomposed

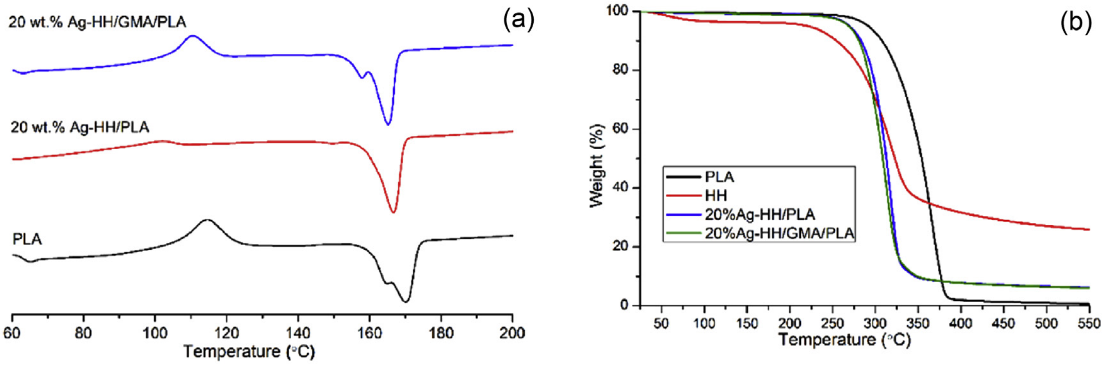

Fig. 3. Thermal properties plotted as (a) DSC curves of PLA and AgNP-HH/PLA biocomposites, (b) TGA curves of PLA, HH and their biocomposites.

in different stages with hemicellulose degrading at 300°C, lignin at 450°C, and cellulose at 550°C [48]. In HH/PLA biocomposites, TGA showed two main degradation regions, where the first region comprises of the thermal degradation of hemicellulose, lignin and cellulose in the HH [49], and the higher temperature region corresponded to the depolymerization of the PLA [50]. The earlier onset of thermal decomposition of the HH/PLA and HH/GMA-g-PLA in comparison to neat PLA indicates that inclusion of HH, which is constituted by low-melting-point lignin and hemicellulose, caused a marginal loss in thermal stability in the biocomposite form.

3.3. Tensile properties

The tensile strength, elastic modulus, and the strain to failure of the neat PLA and the biocomposites are shown in Fig. 4. Fig. 4a shows the tensile strength of the AgNP-HH/PLA biocomposites. Without GMA grafting, the addition of 10 wt % and 20 wt % HH caused a decrease in tensile strength from 65 MPa to 50 MPa, retaining 77% tensile strength of the neat PLA. With 1 wt % GMA grafting at 10 wt % HH, the tensile strength maintained an average of 61 MPa with 94% retention of the neat PLA strength. The addition of AgNP-HH at more than 20 wt % with no GMA caused a further decrease in comparison to the 10 wt % HH biocomposite. The inclusion of HH with PLA over 20 wt % caused inhomogeneous mixing because of a lower specific gravity of HH, and hence causing agglomerates, which are potential stress raisers. The addition of AgNPs to the biocomposites was deemed inconsequential for mechanical property analysis because they are encapsulated within the HH body and hence no contribution to the tensile strength mechanisms was conceivable.

The elastic modulus (Fig. 4b) of the filled biocomposites increased with an increase in the HH content in both uncompatibilized and compatibilized biocomposites in comparison to neat PLA as expected because of the restrictions in chain movement created by the inclusion of the particulate filler [7]. The improvements in the tensile properties in this study are consistent with the trends observed with PLA biocomposites compatibilized with GMA. The tensile strength of GMA-compatibilized biocomposites with rice husk [33], wheat straw [29], and bamboo flour [35] showed increased tensile strength at concentrations of 2–5 wt % of compatibilizer. The tensile strength of the compatibilized biocomposites often matches or exceeds the neat PLA strength, and is greater than the non-compatibilized biocomposite blends. The elastic modulus of the biocomposites with particulate fillers shows increases to a maximum with a concomitant decrease in ductility. In PLA/particulate filler biocomposite blends, the tensile modulus increased with inclusion of GMA compatibilizer [34,35].

The elastic modulus of AgNP-HH/PLA biocomposites, however, showed a critical maximum at 10 wt % HH beyond which the modulus showed a decrease in a manner similar to the elongation behavior at failure. The AgNP-HH/GMA/PLA biocomposite showed opposing trends for increasing HH fraction with the modulus showing an increase, and the elongation showing a decrease. This combination is indicative of the increasing brittleness of the biocomposite with increasing HH content not contributing to tensile strength, and thereby detrimental to the ductility of the biocomposite [51]. Unlike continuous fibers, HH lacks a high aspect ratio to hinder brittle fracture [9,51,52]. Overall, the 20 wt % AgNP-HH/GMA/PLA showed the most advantageous gamut of tensile properties. The tensile strength and the elongation to failure decreased in the uncompatibilized biocomposite because of inadequate load transfer from the matrix to the fiber upon a mechanical input. This inadequacy remedied through compatibilization with GMA grafting. The existing flaws and imperfections in the uncompatibilized biocomposite often cause fracture in semi-crystalline polymers [53] and biocomposites.

The inadequate interfacial adhesion between the fibers and the matrix can be observed from the SEM images of fracture surfaces, shown in Fig. 5a–b. The main components in HH are cellulose, hemicellulose, and lignin, containing large amounts of polar hydroxyl and phenolic hydroxyl groups that lead to sub-par adhesion with PLA causing a decrease in tensile strength in comparison to the neat PLA. In the GMA-g-PLA, the epoxy groups of GMA compatibilizer bond with the hydroxyl groups of the AgNP-HH surface, hence causing the PLA and AgNP-HH to chemically bond at the interface. In Fig. 5c–d, SEM micrographs showed an increase in HH adhesion with the PLA matrix, showing effective AgNP-HH/GMA/PLA compatibility, which is in contrast with the AgNP-HH/PLA biocomposite that shows surface pitting, voids, overall showing brittleness.

3.4. Antibacterial activity

Escherichia coli is a widespread intestinal parasite of mammals. The antibacterial response of AgNP-HH and AgNP-HH/GMA/PLA biocomposite against *E. coli* were explored by a quantitative viable cell counting method.

3.4.1. AgNP-loaded HH antibacterial response

The antibacterial efficiency of the AgNP-HH against *E. coli* is shown in Fig. 6. The bacterial culture was performed in triplicate, with decreasing order of culture populations, with no AgNP loading as control denoted as C1 – C5, and with AgNP loading, denoted as H1 – H5 at equivalent initial culture populations. The number density of bacterial colony for untreated HH after 24 h incubation at different bacterial concentrations was higher than the AgNP-

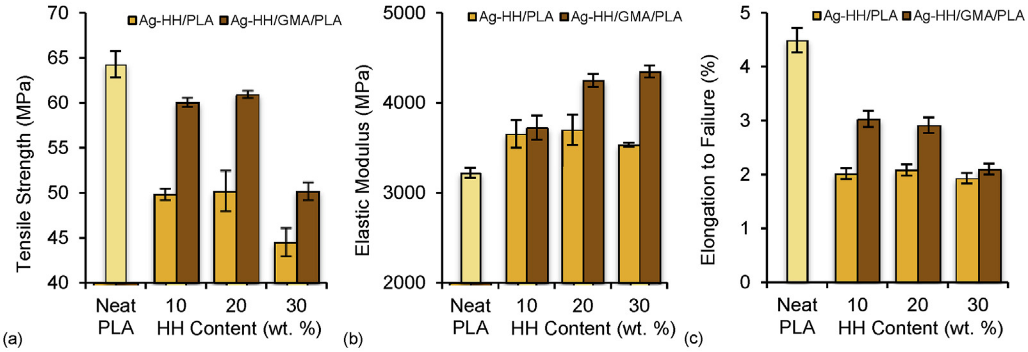

Fig. 4. Tensile properties of neat PLA and filled biocomposites; (a) tensile strength, (b) elastic modulus, and (c) elongation to failure as a function of AgNP-HH content.

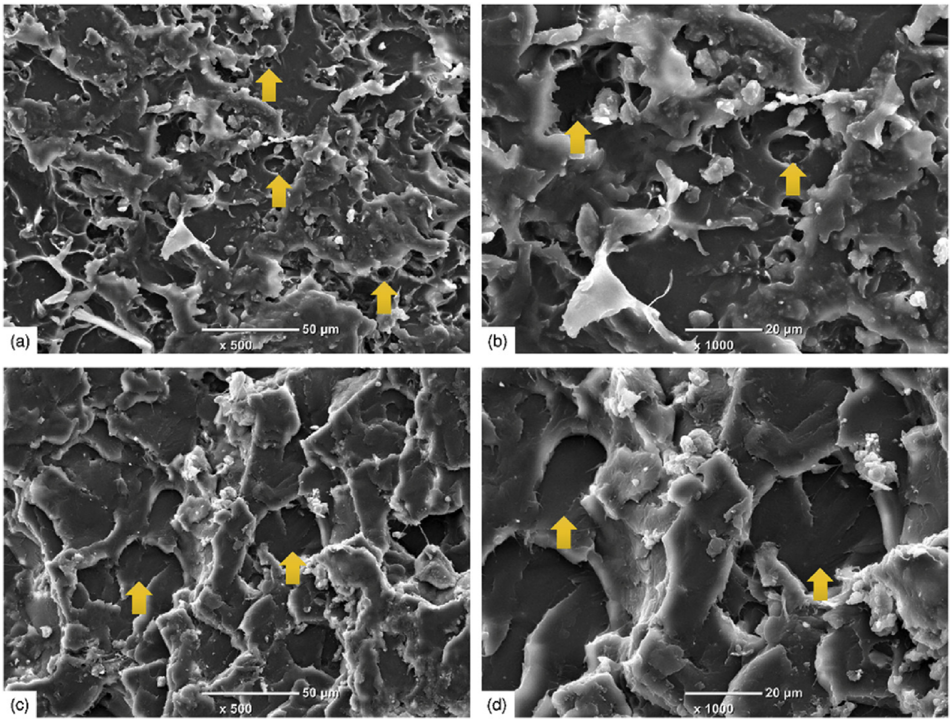

Fig. 5. SEM of fracture surface of (a, b) AgNP-HH/PLA biocomposite, and (c, d) AgNP-HH/GMA/PLA biocomposite.

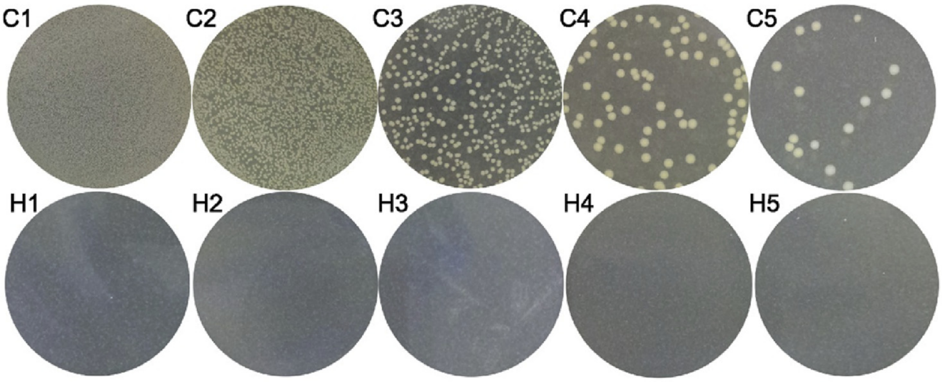

Fig. 6. Antibacterial activity of HH with C1-C5 showing no AgNP loading and H1-H5 showing the presence of AgNPs in HH at equivalent culture levels in descending populations.

loaded-HH sample at all five bacterial levels, whose bacterial count was practically insignificant. This resistance exhibited in the antibacterial tests demonstrated AgNP-HH being clearly antibacterial to *E. coli*. Compared with the control cultures, the antibacterial activity in AgNP-HH can be attributed to the presence of AgNPs in the HH, whose antibiotic mechanisms can be surmised as a synergy of the five pathways, as described in Ref. [18].

The antibacterial action of AgNPs depends on the surface area of nanoparticles. Therefore, this strong antibacterial activity of AgNP-HH is because of the vigorous contact of AgNPs with *E. coli*. The AgNP-HH powder released AgNPs very rapidly and the mechanism of the antibacterial activity of AgNPs likely involves the anchoring of AgNPs to the cell wall or penetration inside the cell and subsequent eradication.

3.4.2. AgNP-HH/PLA biocomposite antibacterial response

The antibacterial activity against *E. coli* is also studied in AgNP-HH/GMA/PLA biocomposites as shown in Fig. 7. The bacteria were incubated in a growth medium with the neat PLA and the biocomposites, and the antibacterial properties of samples were tested using the antibacterial testing standard (ASTM E2149-10). The HH/GMA/PLA without AgNP loading was evaluated as the control sample, whose antibacterial performance is shown in Fig. 7a. The number density of bacterial colony for HH/GMA/PLA biocomposites with untreated HH was high, with no conceivable antibacterial activity. The HH/GMA/PLA biocomposites with AgNP loaded HH (Fig. 7b and c) with 0.025 wt % and 0.05 wt % of AgNPs showed a decrease in the CFU/mL from 62 for the HH/GMA/PLA biocomposite, to 9 and 7 for 0.025 wt % AgNP and 0.05 wt % AgNP-HH/GMA/PLA biocomposites, respectively. These antibacterial responses correspond to *E. coli* reduction in CFU/mL of 85% and 88%. The benefit of adding AgNPs to HH/GMA/PLA brings about evident antibacterial ability against *E. coli* in the HH/GMA/PLA biocomposites. Further to the known effectiveness of AgNPs on gram

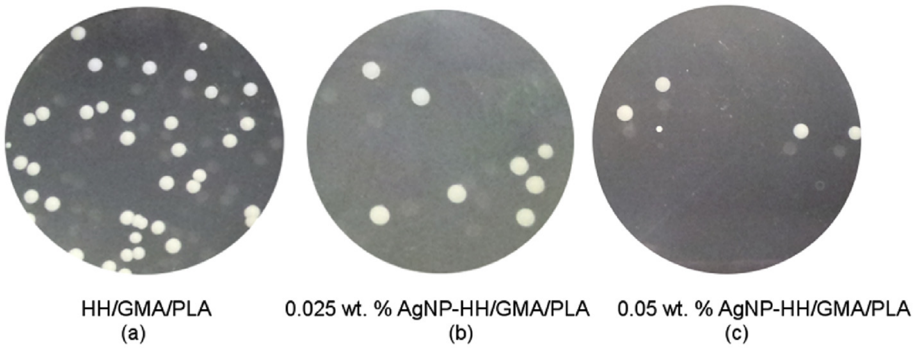

Fig. 7. Comparison of the antibacterial ability of a) HH/PLA b) AgNP-HH/GMA/PLA (0.1% AgNP in HH) and c) AgNP-HH/GMA/PLA (0.2% AgNP in HH).

positive bacteria such as *S. aureus* [54], this study supports their antibacterial efficiency on gram negative bacteria as *E. coli* as well.

Although it is believed that AgNPs are solely responsible for the antibacterial activity of HH//GMA/PLA biocomposite, there is a substantial contribution of HH powder to enhance the antibacterial efficiency [55]. The HH powder promoted AgNPs release, i.e., the HH powder allowed more AgNPs to migrate onto the HH/GMA/PLA biocomposite surface. Since HH is very hydrophilic in nature, incorporation of HH in PLA makes the biocomposite increases the hydrophilicity as well, hence more water molecules are absorbed by the biocomposite, which facilitates the migration of AgNPs on to the PLA surface, and eventual contact to *E. coli*. This contact is necessary to enable the antibacterial effect shown the AgNPs on the tested bacteria.

3.5. Silver migration into food simulants

The heavy metal migration limits from food packaging materials are subject to strict regulations worldwide. The European Union legislation 2002/72/EC sets the limits of migration through guidelines in 82/711/EEC. The maximum metal concentration of general substances migrating from the packaging materials in the selected food simulants for a certain migration time for metals may not exceed 60 mg/kg or 10 mg/dm^2.

The initial concentration of Ag in the AgNP-HH/PLA biocomposite was 46.65 mg/kg. The concentration of the AgNPs in simulant was calculated by Equation (2).

$$M_{\text{food simulation}} = M_{\text{packaging}} \times \text{Migration Ratio} \tag{2}$$

The migration ratios of AgNPs from AgNP-HH/PLA biocomposite are shown in Fig. 8. The maximum migration ratios in aqueous acetic acid were 6.6% and 5.1% at 40°C and 70°C respectively, while in aqueous ethanol, the maximum migration ratios achieved were 0.45% and 0.47% at 40°C and 70°C, respectively.

The calculated silver content in the food simulants was within the range of 0.20–3.08 mg/kg, which was lower than the European Union (EU) legislation limits of 60 mg/kg and 10 mg/dm^2.

Many packaging materials with silver nanoparticle additive are now commercially available [56]. In polyolefin based food packaging materials, the antimicrobial nano-silver migration to food simulants (50% v/v ethanol and 3% v/v acetic acid) [57] showed an increase with increasing time and temperature. In PLA films, silver-based nanoclay and silver nanoparticle-loaded cellulose nanocrystal antimicrobial agents [13,58] showed accelerated migration of silver in a slightly acidic aqueous medium, indicating plasticization and/or partial acid hydrolysis of the PLA films. Overall, the extent of migration is a function of the food simulant, migration time, and temperature. The AgNP migration behavior from the AgNP-HH/PLA biocomposite surface was different with the two food simulants. The amount of AgNP migration was higher in 3% (v/v) aqueous acetic acid than that in 95% (v/v) aqueous ethanol, which is expected because AgNPs dissolve with relative ease in an acidic solution than in organic solutions and alcohols such as aqueous ethanol, which show limited AgNP solubility. The solubility of AgNP in aqueous acetic acid increases as the temperature rises, which causes an increase in migration of AgNPs in this simulant. Certain organic chemical additives (such as plasticizers, stabilizers, etc.) in the plastic may also migrate into aqueous ethanol and further reduce the solubility of AgNPs. These underlying factors control the migration behavior of AgNPs in food simulants. Overall, both antibacterial resistance and acceptable heavy metal migration were achieved with the AgNP-HH/GMA/PLA biocomposites.

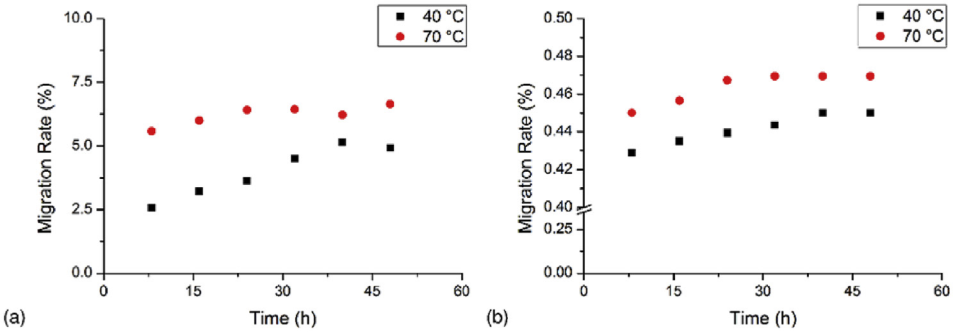

Fig. 8. Migration of Ag from biocomposites into a) 3% (v/v) aqueous acetic acid and b) 95% (v/v) aqueous ethanol.

4. Conclusions

A silver nanoparticle antibacterial agent was successfully loaded into hemp hurd filler confirmed through SEM imaging and XRD crystallinity analysis. The silver nanoparticle-loaded hemp hurd was compounded with PLA as an AgNP-HH/GMA/PLA biocomposite is potentially cost-effective, yet retains a majority of tensile mechanical properties of the neat PLA. GMA grafting on to PLA was beneficial for the mechanical properties and interfacial adhesion in the AgNP-HH/GMA/PLA biocomposites. The AgNP-HH and AgNP-HH/PLA biocomposites demonstrated antibacterial resistance against *E. coli*, showing promise as an antibacterial, biodegradable packaging material. Silver migration to the food simulants determined using ICP-OES was 0.20–3.08 mg/kg, which meets the European Union (EU) legislation (2002/72/EC), substantially lower than the permitted value of 60 mg/kg. However, the role of AgNPs in the elasticity of the HH filler is critical for further understanding the thermal/mechanical mechanisms of the biocomposite, and such an investigation constitutes future work by the authors.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.compositesb.2016.06.022.

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4.4 Paper-VI: Assessing Technical and Financial Viability of a New Generation Antibacterial Biocomposite: The Case of Food Packaging Industry

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The objective of this article was to assess the technical and financial viability of the antibacterial biocomposite produced with poly(lactic acid) and silver nanoparticles loaded hemp hurd for food packaging. The overall contribution of this article in this thesis is to provide data on the degree and magnitude of uncertainties related to investment to afford better product design, and establish the potential of PLA-industrial hemp biocomposites for food packaging applications.

Assessing technical and financial viability of a new generation antibacterial biocomposite: The case of food packaging industry

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Abstract:

Polylactide biocomposites are potentially biodegradable and thermo-mechanically stable packaging materials that utilize biomass fillers and silver nanoparticles. However, biodegradable biocomposites for packaging are relatively contemporary, and require establishment of commercial viability for market entry. To that end, the financial and technical viability of polylactide based biocomposites with industrial hemp hurd loaded with antibacterial silver nanoparticles is investigated and presented. Firstly, the biocomposite technical viability is assessed for mechanical and thermal performance in food packaging. The addition of glycidyl methacrylate assisted in tensile and flexural strength improvements in comparison to neat polylactide. Strong antibacterial activity was achieved against gram-negative *Escherichia coli* through addition of silver nanoparticles, and the silver and heavy metal migration behavior in food simulants was deemed to be at safe for food contact. Secondly, a cost-benefit analysis was performed to assess viability in commercial manufacturing for producing rigid food packaging. Financial analysis revealed the benefit/cost ratio at 6% discount rate as 1.63, indicating the project is feasible. The results of sensitivity analysis conducted to identify risks and uncertainties using various scenarios that affect viability supported biocomposite production to be sustain in adverse financial conditions. The biocomposite sensitivity and financial analyses provide data on the degree and magnitude of uncertainties related to investment to afford better product design, and establish the potential of PLA-industrial hemp biocomposites for food packaging applications.

Keywords: *A. Polymer-matrix composites (PMCs), B. Mechanical Properties, C. Statistical properties/methods, E. Injection Moulding, Food packaging, Cost benefit analysis*

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1 Introduction

The ever increasing interest in bioplastics development [1-3] is intensifying with biocomposites with natural fibres/fillers emerging as candidates for food packaging [4-6]. The research and development of biocomposite technologies is focused on lowering costs and optimizing the performance of such bio-based packaging [7-9]. Simultaneously, environmental concerns are causing greater interest in utilizing agricultural and forestry resources as alternative feedstocks [10-12], often in new market sectors including food packaging, a highly competitive area driven by performance maximization and cost minimization.

The overarching goal of a food packaging material is containing food in a cost-effective way that satisfies industry requirements and consumer desires, maintaining food safety, and minimizing its environmental impact [4]. The knowledgeable selection of packaging materials and technologies assists in retaining food product quality and freshness during distribution and storage. Plastics, paper, glass and metals are prevalent as traditional food packaging materials, while rigid and flexible plastic packaging hold the highest market share of 37% by value [13].

Recycling of plastic food packaging materials is impracticable as they are contaminated by foodstuff and biological substances after use and cannot be reclaimed in an economically viable [6] manner, often leading to landfilling [14], which is a growing environmental concern. This recycling dilemma is causing the market to shift towards selection of eco-friendly materials, which are also safe for use. Biodegradability/compostability thus materialized as a functional requirement for food packaging, as well as a legislative requirement, and is allowing the food packaging producers to develop biocomposites with biodegradable polymers and natural fibres, as they allow complete degradation in soil through composting, with negligible toxic or noxious emissions [15]. Hence, combining natural fibres and fillers with biodegradable or compostable polymers offers significant environmental benefits [16] as biocomposites.

Among the biodegradable/compostable polymers, polylactide (PLA) is recognized [17] for industrial thermoplastic applications because of its processability ease [16]. PLA is a strong candidate to replace conventional petroleum-based polymers, and often possesses higher mechanical properties, and greater versatility in process selection [16, 18-20]. In recent years, considerable research effort has been devoted to the development of new eco-friendly, sustainable bioproducts using PLA, including biocomposite applications for automotive, building, and appliance industries. PLA has been used in food packaging research and development [21], because it is deemed safe for use in food contact [22].

Synthetic and bio-based fillers are often added to polymers to lower cost at acceptable physical and mechanical properties. However, the supply of natural resources is depleting, and demand for renewable raw materials is increasing, therefore, responsible use of available natural fibres and fillers is critical for sustainable development. Plant co-products that avoid the use of new agricultural lands, preclude competition with food sources, and provide value addition to farmers [23], are highly desirable. For instance, industrial hemp fibers are used as a composite reinforcement [24] because of their high specific mechanical properties, however, hemp hurd, a co-product of the industrial hemp fiber production as a biocomposite filler is evolving [25]. The application of industrial hemp hurd as a filler for biocomposites not only adds value to the material, but also addresses environmental concern associated with plastic recycling [26].

Industrial hemp hurd bears substantial potential for compounding with PLA as biocomposites for use in food packaging applications. A previous study by the authors indicated industrial hemp hurd possesses antibacterial activity against *Escherichia coli* [27]. However, the performance of industrial hemp hurd as a constituent in PLA-based biocomposites is relatively unknown, and often overshadowed by bast fibres such as industrial hemp, sisal, jute and kenaf whose utilization has reached in the recent past [28] to a pilot/commercial scale. The mechanical and other technical aspects of natural fiber/filler-reinforced composites are extensively studied and reported in the literature. However, the translation of research and development into industrial products by gaining customer and manufacturer confidence in novel bio-based fillers can be established through comprehensive financial analysis.

However, there is a lack of studies on economic evaluations in the literature, except the cost benefit analysis of PLA production [29] in Thailand, and industrial hemp production [30] in New Zealand. Given the potential of PLA production and growing industrial hemp in Australia, it is of significance for the industry and policy makers to examine its financial viability. Establishing the financial viability and creating new avenues of value added utilization of industrial hemp will cause in increased production, and ultimately cause a lowering the cost of hemp hurd, as the hurd constitutes 70% of the hemp stem [31].

In this research, an antibacterial biocomposite was produced using extrusion/injection moulding with silver nanoparticles (AgNPs) encapsulated in hemp hurd filler, and PLA as the polymer matrix, grafted with glycidyl methacrylate as a polymer/filler interfacial compatibilizer. Initially, the technical viability was analyzed through investigations of mechanical, thermal, antibacterial and migration behavior of the biocomposite. Then, financial aspects of the developed antibacterial biocomposite were assessed by applying the economic analysis tool (cost benefit analysis) for determining the potential of the biocomposite for food packaging in Australia. The specific objectives of this study are to (a) assess the technical viability of the biocomposite with respect silver nanoparticles loaded hemp hurd as an antibacterial agent as well as a structural filler, and (b) conduct a cost benefit analysis of the biocomposite production based on the assumptions that this biocomposite is an alternative to the existing plastic food packaging.

2 Methodology

2.1 Materials and composite fabrication

PLA resin (4032D) with density of 1.24 g/cm^3, melting range of 155 °C – 170 °C was purchased from NatureWorks, LLC (Minnetonka, MN), and retted industrial hemp hurd (HH) powder with a mean particle size of 40 ± 10 μm was obtained from Ecofibre Industries Operations (EIO) Pty Ltd, Australia. The bi-functional monomer glycidyl methacrylate (GMA) and an initiator *tert*-butyl perbenzoate (TBPB) for the grafting reaction were supplied from Aladdin Chemistry Co., Ltd. and were used with no further purification. The silver nanoadditive antibacterial agent was synthesized and loaded into the HH filler (AgNP-HH) using a proprietary method developed in collaboration with EIO Pty Ltd.

The PLA resin granules and AgNP-HH powder were dried under vacuum at 80 °C for 24 h. Neat PLA, AgNP-HH/PLA, and AgNP-HH/GMA/PLA were blended in melt stage using a conical twin screw extruder (Ruiming Plastics Machinery, Wuhan, China) with at 40 rpm and at 175 °C for a duration of 10 min. The extrudate was granulated, and then injection molded into standard test specimens using an injection molder (SZ-15, Wuhan, China) with injection pressure of 3 MPa, 200 °C temperature, and 30 s cycle time, and mold cavity temperature of 40 °C.

2.2 Properties assessment

The mechanical properties of the biocomposites upon tensile loading were determined through testing on an Instron 5567 load frame using GB/T 1040.1-2006 standard. The biocomposite impact properties was determined using ISO179-1: 98 standard on an impact tester (XJ-50Z, Chengde Dahua Testing Machine Co. Ltd., Chengde, China). The mechanical properties in flexural or bending were determined on an Instron 5567 instrument according to ISO 178: 2010 standard, using a crosshead speed of 10 mm/min. All mechanical property values presented are the average of five replicated tests.

The thermal response characteristics of the biocomposites were characterized by a differential scanning calorimetry (DSC) on a Mettler Toledo TGA/DSC1 analyzer (Mettler-Toledo, Switzerland). The specimens were conditioned at 30ºC for 1 min before heating to 200ºC at a rate 10ºC/min, dwelled for 3 min and cooled down to 30ºC at a rate of 25ºC/min. After 1 min at 30ºC, a second scan from 30ºC to 200ºC at a rate of 10ºC/min was performed. A thermogravimetric analyzer (TGA) was used to evaluate thermal stability of the neat PLA and the biocomposites through decomposition analysis. TGA was conducted using 2 mg to 3 mg sample at a heating rate of 20 °C/min in temperature range of 25°C to 550°C.

The antibacterial performance on *Escherichia coli* (ATCC # 25922) strain was analyzed through bacterial cultures maintained on nutrient agar slopes. The antibacterial performance of the AgNP-HH and biocomposite was investigated according to ASTM E2149-10 standard. The migration testing for the biocomposite and filler materials was conducted according to guidelines of the European Council Directive 82/711/EEC with two food simulants, i.e., 3% (v/v) aqueous acetic acid and 95% (v/v) aqueous ethanol. Combined, these simulants correspond to a range of alcoholic, aqueous, and acidic foods that may be in contact with the biocomposites. The migration of AgNP was established at oven temperature of 40 °C and 70 °C. At designated intervals, the migration into the simulants was recorded, followed by analysis on a Perkin Elmer Optima 2100 DV inductively coupled plasma optical emission spectrometer.

2.3 Financial Viability

The financial viability of producing the biocomposite with GMA-grafted-PLA reinforced with AgNPs filled HH was determined through the analysis of costs of a common production operation, and the financial benefits from the usage of these materials in food packaging.

2.4 Stages of the cost benefit analysis

Cost-Benefit Analysis (CBA) was applied as a tool for evaluating the financial viability of the investment. CBA has been employed to evaluate the scenarios of biocomposite production with regard to different cost and benefit conditions. The conduct of this study follows the five step procedures, i.e., (1) identification of technological parameters, (2) determination of the investment cost and benefit components, (3) calculation of the present value of costs and benefits, (4) quantitative estimation of financial evaluation indicators, and (5) making a recommendation [32].

The technical characteristics of the investment under evaluation, which relate to capacity, efficiency, qualitative and quantitative characteristics of inputs, and outputs are recorded in detail. The analysis involves initially the recording of the relevant cost and benefit components, which determine the financial return of the investment under study. These components are determined based on market data and previous experience. On the contrary, costs and benefits resulting from the changes in environmental quality or other social goods are difficult to measure, especially in the case of non-tradeable goods, such as soil quality improvement through heavy metal absorption by hemp plants, or CO_2 emission reduction. The time allocation of the cost and benefit components over the life cycle of the examined project also affects the results of the analysis.

CBA was used to assess, quantify and value the potential project strategies within the framework of this research. The net present value (NPV) and the benefit cost ratio (BCR) were estimated using the following criteria [33]:

$$NPV = \sum_{t=1}^{n} \frac{(B_t - C_t)}{(1+r)^t} \tag{1}$$

$$BCR = \frac{\sum_{t=1}^{n} \frac{(B_t)}{(1+r)^t}}{\sum_{t=1}^{n} \frac{(C_t)}{(1+r)^t}} \tag{2}$$

where, *B*, *C*, *r* and *t* refer to benefit, cost, discount rate and time frame of the project, respectively.

The time span of the analysis was considered as 10 years, since most of the impacts are likely to be observed in the first few years after establishment of the project, although the majority of the costs and benefits are continually realized. The sensitivity analysis was executed using discount rates ranging between 3% and 10%. The discount rate was assumed to be 6% for the base-case scenario, 10% for the pessimistic scenario, and 3% for the optimistic scenario. Using the steps described above, the interpretation of the results of the CBA be made with recognition of the principle of what the tool offers, as well as the limitations in application.

2.4.1 Numerical data and assumptions

Data on benefits and costs of this investment were obtained from both primary sources and secondary sources- published papers and/or unpublished documents. Primary data were collected through interviews and telephone conversations with key stakeholder (Ecofibre Industries Operations Pty Ltd), industrial machinery suppliers, and food packaging manufacturers. All the cost and benefit items used to determine the monetary value of the CBA calculations are summarized in **Table** *1*.

Table 1. Summary of the Cost and Benefit Items in the Project

Cost & benefit items	Quantity	Description
Building rent	700 m^2	Floor space for production, warehousing and office
Silver loading process	10 sets	Each set offers 50 kg AgNP-HH production per day
Dryer	8 units	Total capacity 2000 kg
Extruder	2 sets	Production capacity 1600 kg
Injection molder	3 sets	Production capacity 1500 kg
Miscellaneous	As required	Forklift, testing equipment, and tools
Raw materials and energy	As required	PLA resin, hemp hurd powder, chemicals for AgNP synthesis, compatibilizer and initiator, water, and electricity
Other associated costs	As required	Repair and maintenance, packing and transportation
Manpower	9 employees	Production and maintenance, administration and management
Sale of product	1 ton per day	About 70% of total production capacity was utilized

The daily production was assumed as 1 ton (260 tons per year), which is 70% of actual production capacity. AgNP-HH/GMA/PLA (20 wt. % AgNP-HH and 1 wt. % GMA) biocomposite production from raw materials which is a realistic case, is considered. This study assumes a time horizon of 10 years, with 6 months of the first year allocated for establishment of the facility. Thus, it is assumed that production starts after the establishment period. For the purpose of this parametric study, the establishment and operation of a factory with a production capacity of 1500 kg per day is assumed. Preparation of AgNP-HH from HH requires 10 sets of equipment with production capacity of 50 kg AgNP-HH per day per module. Thus, the total AgNP-HH production capacity is 500 kg per day. The drying unit comprises of 8 dryers with total 2000 kg raw materials drying capacity. Two sets of twin screw extruder with production capacity of 800 kg per hour per set is placed in extrusion unit. Injection molding unit is constituted by three injection molders with 1500 kg production capacity per day. All the processing units require 400 m^2 floor space, collectively. The total required floor space is assumed to be 700 m^2 (including the processing, warehousing and administration units). To ensure realistic raw materials planning, a 30% loss of raw materials is included in each stage of processing, i.e., AgNP-HH production, extrusion and injection molding. A 2% inflation has been considered for each year in the calculations.

3 Results and Discussion

3.1 Technical Viability

The AgNP loading on the HH was confirmed through XRD analysis on the AgNP-loaded HH and the PLA and unfilled HH counterparts in a previous studies by the authors [34]. The deconvolution of Ag planes in the XRD patterns of AgNP-loaded HH supported the presence of AgNP loading in the filler. The AgNP loading levels of 0.025 wt % and 0.05 wt % were designed for the biocomposites.

3.1.1 Mechanical properties

The tensile strength, elastic modulus, the strain to failure, flexural strength, flexural modulus and impact strength of the neat PLA and the biocomposites are presented in **Table** *2*. For the purpose of mechanical property analysis, the addition of AgNPs to the biocomposites as bonded to the HH was deemed inconsequential because they are encapsulated within the HH body, showing insignificant contribution towards tensile strength development. The addition of AgNP-HH to the PLA matrix significantly reduced the tensile and flexural strength of the biocomposites, compared with the unfilled PLA. The notched impact strength decreased with increasing AgNP-HH content as well, which is expected of biocomposites with lignocellulosic fillers. The inability of the AgNP-HH with irregularly-shaped particles to carry stresses transferred from the PLA matrix and inadequate interfacial bonding resultant of voids created at the AgNP-HH/PLA interface, leads to a weak structure [35] and subsequently, lower impact energy absorption at failure. However, the tensile/flexural mechanical strength was significantly improved in comparison to the non-compatibilized biocomposite when PLA was grafted with GMA, providing greater compatibility and interfacial bonding between PLA and HH filler.

With 1 wt. % GMA grafting at 20 wt. % AgNP-HH loading, the tensile and flexural strength maintained an average of 61 MPa with 95% retention, and 93 MPa with 90% retention of the unfilled PLA strength respectively. The inclusion of AgNP-HH with PLA exceeding at 20 wt. % caused inhomogeneous mixing because of a lower specific gravity of AgNP-HH, and hence causing agglomeration in the blend. The addition of GMA at the 10 wt. % AgNP-HH caused an average impact strength of 3.1 kJ/m^2, which is higher than neat PLA (2.99 kJ/m^2). The impact strength data demonstrated that the addition of GMA possesses the potential of improving physical and mechanical properties of AgNP-HH/PLA composites.

Table 2. Mechanical Properties of PLA and Biocomposites

Composition	Tensile strength (MPa)	Young modulus (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (KJ/m^2)
PLA	64.27±1.43	3221.60±57	4.49±0.13	103.03±1.9	3852.88±51	2.99±0.06
PLA/10 wt.% AgNP-HH	49.85±0.63	3655.42±156	2.02±0.07	82.72±2.4	3968.51±93	2.57±0.29
PLA/20 wt.% AgNP-HH	50.22±2.25	3699.28±167	2.09±0.04	83.51±4.1	4170.96±109	1.73±0.39
PLA/30 wt.% AgNP-HH	44.52±1.58	3535.09±23	1.93±0.11	58.86±5.3	5161.12±67	1.07±0.38
PLA/1 wt.% GMA/10 wt.% AgNP-HH	60.06±0.51	3722.79±135	3.03±0.17	95.65±2.1	4947.76±78	3.09±0.13
PLA/1 wt.% GMA/20 wt.% AgNP-HH	60.95±0.39	4249.94±72	2.92±0.05	93.33±2.7	5023.19±157	3.02±0.18
PLA/1 wt.% GMA/30 wt.% AgNP-HH	50.18±0.96	4349.93±66	2.10±0.07	80.59±6.3	5288.50±136	2.38±0.17

The addition of AgNP-HH to the PLA matrix significantly increased its elastic and flexural modulus in both uncompatibilized and compatibilized form in comparison to neat PLA, as expected, because of the restrictions caused in PLA chain movement because of the inclusion of the particulate filler [15]. The inclusion of AgNP-HH, a mechanically elastic particulate to the plastic PLA [36] causes restricts chain movement and hence shows a higher stiffness in the biocomposite form in comparison to the neat polymer, which shows higher ductility at an equivalent stress.

3.1.2 Thermal properties

The thermal properties of the PLA and the biocomposites obtained from DSC are shown in **Table** *3*. Often, the addition of AgNP-HH and GMA affect the recrystallization of base PLA, with the AgNP-HH acting as a nucleating agent PLA [37], accelerating recrystallization, essential for accelerating production cycles [38]. The retention of the T_g with a 3.5% change, lowering of crystallization temperature by 8°C, and moderate change in melting temperature by 4.5°C with respect to the neat PLA, support the implementation of traditional thermoplastic processing methods and hence would not warrant re-engineering of the processing/production commercial parts made using these biocomposites blends.

Table 3. Thermal Characteristics of PLA and Biocomposites

Composition	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_f (J/g)	X_{DSC} (%)
PLA	62.6	114.7	170.3	17.4	29.6	13.1
PLA/20 wt.% AgNP-HH	61.0	102.0	166.0	2.1	25.7	31.8
PLA/1 wt.% GMA/20 wt.% AgNP-HH	60.2	110.6	165.0	12.0	27.0	20.5

Thermal degradation properties of the neat PLA and the biocomposites are shown in **Table** *4*. The AgNP-HH shows thermal degradation in two stages, i.e., (1) initial 6–8% of weight loss because of residual moisture in the lignocellulosic filler, and (2) above 250 °C, where AgNP-HH shows decomposition through to 350–360 °C, involving hemicellulose, lignin and cellulose degradation [39]. Within two main decomposition regions, the first region is comprised of the thermal degradation of hemicellulose, lignin and cellulose in the HH [40], and the higher temperature region related to the depolymerisation of the PLA [41]. The earlier thermal decomposition onset of the AgNP-HH/PLA and AgNP-HH/GMA/PLA in comparison to unfilled PLA suggested AgNP-HH causing a minor loss in thermal stability of the biocomposite.

Table 4. Thermal Stability Characteristics Determined from TGA

Specimen	T_5 (°C)	T_{50} (°C)	T_{max} (°C)	Residue (%) at 550°C
PLA	291	354	367	0.6
AgNP-HH	221	322	322	25.9
PLA/20 wt.% AgNP-HH	269	308	312	6.1
PLA/1 wt.% GMA/20 wt.% AgNP-HH	269	312	318	6.2

3.1.3 Antibacterial activity

E. coli is a gram negative bacteria found in the intestines of mammals, and a common testing strain used to determine the antibacterial effectiveness of antibiotic chemicals. The addition of AgNP to the HH showed enhanced antibacterial activity, confirmed through viable cell counting of the bacterial colony forming units (CFU). The AgNP-HH/GMA/PLA biocomposites resisted the growth of *E. coli* at five concentrations ranging from 1.5-3.0 × 10^5 to 1.5-3.0 × 10 CFU/mL.

The number of bacterial colonies for untreated HH incubated for 24 h were higher than AgNP-loaded-HH at all concentrations. The AgNP-HH showed clear antibacterial activity against *E. coli,* when compared to the control, exhibiting antibiotic mechanisms, which adopt a pathway as described in Ref [42].

The bacterial colony growth for HH/PLA biocomposites with untreated HH was high, with weak antibacterial activity. The AgNP-HH/GMA/PLA composites with AgNP loaded HH with 0.025 wt. % and 0.05 wt. % of AgNPs showed a decrease in the CFU per unit volume from 62 CFU/mL for the HH/PLA biocomposite, to 9 CFU/mL and 7 CFU/mL for 0.025 wt. % AgNP and 0.05 wt. % AgNP loaded biocomposites, respectively. These antibacterial responses correspond to *E. coli* CFU/mL reduction of 85% and 88% respectively. The benefit of adding AgNPs to HH/PLA brings about evident antibacterial ability against *E. coli* as biocomposites. Further to the known effectiveness of AgNPs on gram positive bacteria such as *S. aureus* [43], this study supports their antibacterial efficiency on gram negative bacteria as *E. coli* as well.

AgNPs can be attributed with a majority of antibacterial activity in AgNP-HH/GMA/PLA biocomposite, the HH also contributes to the antibacterial efficiency [44] as a standalone filler. The HH powder, however, in the current case are restricted as delivery media for promoted AgNPs release, i.e., the HH powder allowed more AgNPs to migrate onto the HH/PLA composite surface. Since HH is hydrophilic in nature, incorporation of HH in PLA increases the biocomposite hydrophilicity in comparison to neat PLA, hence more water molecules are absorbed by the biocomposite facilitating the migration of AgNPs to the PLA surface, and direct contact with *E. coli*. The antibacterial effectiveness of AgNPs in the biocomposite, on the tested bacteria supported the aforementioned theory.

3.1.4 Migration of silver and heavy metals

For food packaging applications, strict regulations control the heavy metal migration limits from packaging materials. For example, the European Union legislation 2002/72/EC sets the limits of migration through guidelines in 82/711/EEC. The maximum heavy metal concentration of general substances migrating from the packaging materials in selected food simulants for a certain migration time for metals may not exceed 60 mg/kg or 10 mg/dm^2 [45]. In this section, the silver and other heavy metals migration from the biocomposite are presented.

The antibacterial biocomposite had the initial Ag concentration of 46.65 mg/kg. The migration rate is calculated using Equation 3.

$$Migration\ rate\ (\%) = \frac{\mathrm{M}_{food\ simulant}}{\mathrm{M}_{packaging}}\ X\ 100 \qquad (3)$$

The migration data of AgNPs from the biocomposite are presented in Figure *1*. The migration observed in aqueous acetic acid, which were 6.6% and 5.1% at 40 °C and 70 °C respectively, while in aqueous ethanol, the highest migration rates were 0.45% and 0.47% at 40 ºC and 70 ºC, respectively.

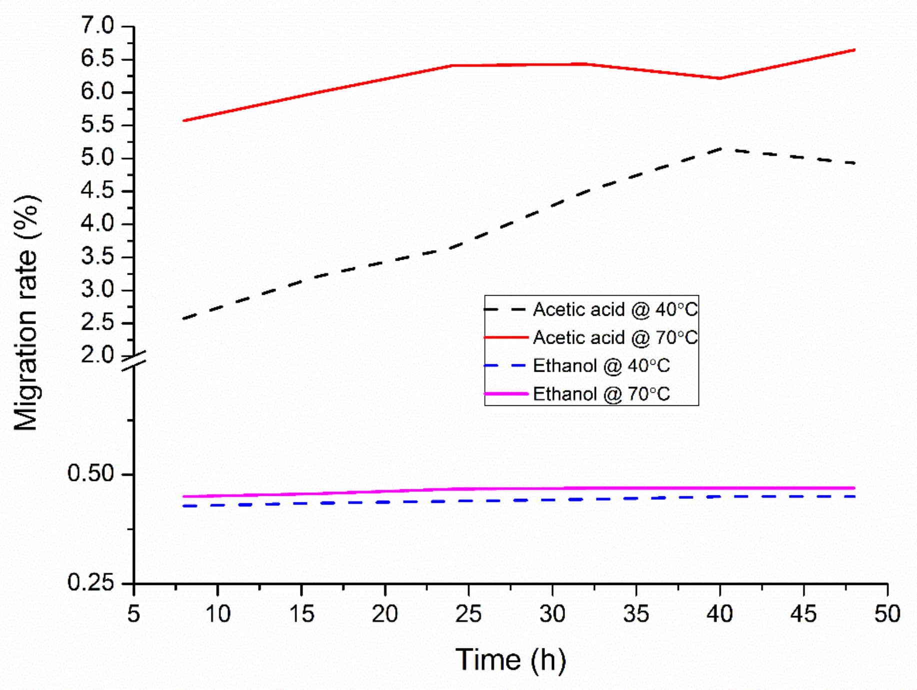

Figure 1. Migration of AgNP from Biocomposites into Food Simulants

In all cases, the calculated AgNP content in the food simulants was within the range of 0.20 – 3.08 mg/kg, which meets the European Union (EU) legislation limits of 60 mg/kg and 10 mg/dm^2. The food simulant, migration time, and temperature dictate the degree of silver particle migration from food packaging [44]. The overall AgNP migration was higher in 3% (v/v) aqueous acetic acid over 95% (v/v) aqueous ethanol because of the limited AgNP solubility [3, 46]. With an increase in temperature, the AgNP solubility in aqueous acetic acid increases as well, and hence the overall migration at 70°C is higher over 40°C. Organic additives including plasticizers and stabilizers also migrate ethanol lower the solubility of

AgNPs. The migration of AgNPs in food simulants is resultant of the aforementioned mechanisms.

The industrial hemp crop absorbs heavy metals from soil inherently, and [47] hence the analysis of migration of such heavy metals including Ni, Cd, Pb, and Cr is imperative for food packaging biocomposites. **Table** *5* shows the migrated amount of heavy metals (Ni, Cd, Pb, and Cr) from the biocomposite in food simulants at 70 °C for 48 hours. The migration values of heavy metals is practically negligible, and bears no health risk to food in contact. Thus, using HH, which is loaded with heavy metals in HH/PLA biocomposite does not bear a negative effect on food safety because of high retention within the HH structure, and consequent low migration to food.

Table 5. Migration of Heavy Metals in Food Simulants at 70°C after 2 Days Absorption

	Ni (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Cr (mg/kg)
Acetic Acid (3% v/v)	0.013	0.002	0.004	0.199
Ethanol (95% v/v)	0.012	0.002	0.003	0.147

Many heavy metals are capable of imparting antimicrobial activity in food packaging plastics. However, Ag-based nanoparticles are a particularly effective solution for a diverse range of plastics for this purpose. However, the main concern with the usage of nanoscale additive in plastics without encapsulation is the ready migration into foodstuffs, which causes adverse toxic effects on human physiology. The encapsulation of AgNPs in HH specifically is a way of precluding excessive nanoparticle migration into food and subsequently affect human physiology.

3.2 Assessing Financial Viability

3.2.1 Financial analysis of the project and discussion

The results of the financial analysis of the project are presented in the integrated cost-benefit framework, where the comprehensive monetary values of associated costs and benefits resulting from the sales of product are considered, and outputs are compared with the inputs. The cash flow of the project by year is shown in Figure *2*. The net benefit remained positive throughout the total life span of the project except in the first year, where the cost of establishment of the biocomposite production exceeds the overall benefits derived.

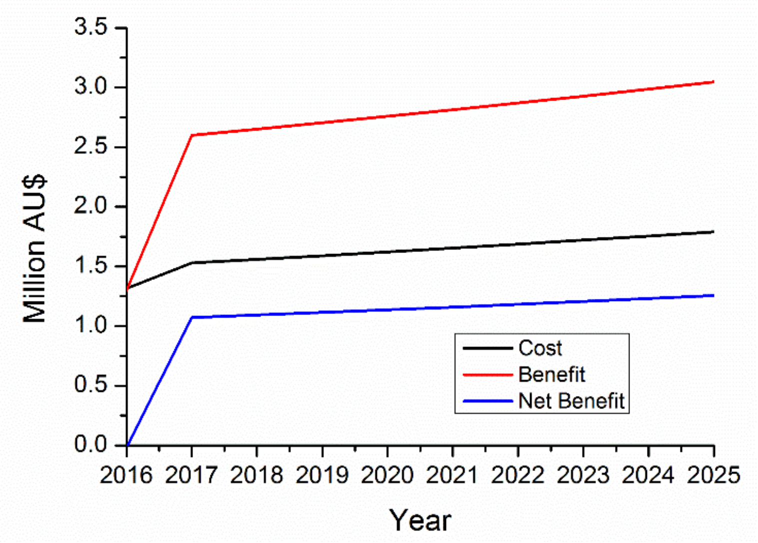

Figure 2. Cash flow of antibacterial biocomposite food packaging (by year)

The total benefits from the sales of the product is calculated to be AU$ 26.67 million. The total cost of the investment is projected to be AU$ 16.24 million, including an investment cost of AU$ 1.23 million. The investment cost by major investment categories and benefits are summarized in **Table** *6*.

Table 6. Cash Flow of Antibacterial Biocomposite Food Packaging (Million AU$)

Components	**Total (Million AU$)**
Cost	
Investment costs	
- Building rent	0.71
- Equipment	0.52
O&M	
- Raw materials and energy	9.60
- Maintenance and other associated costs	0.61
- Manpower	4.80
Total cost	16.24
Benefit	
- Sale of product	26.67
Total Benefit	26.67
Net Benefit	**10.43**
NPV @6%: $7.38 million	
BCR @6%: 1.62	

As the NPV is positive up to a discount rate of 6%, the present value of the benefits exceeds the present value of the costs, and hence the investment is deemed viable. A higher NPV and

BCR infer a more financially feasible project, and BCR indicates the magnitude of the benefits relative to the cost of a project. Therefore, if the estimated BCR is greater than 1, the project is considered to be viable.

Financial analysis revealed that the BCR at 10% discount rate is 1.61, which indicates that the investment is also viable. Furthermore, this investment would cut the landfill burden as well as offer incentives for industrial hemp growers. For instance, since the product is compostable and then biodegradable, a landfill disposal (about 2500 ton) cost of AU$ 0.27 million is expected to be saved by the period of 10 years [48].

3.2.2 Assessing uncertainties and risks

The reliability of the expected NPV from a CBA is a common financial tool, albeit sensitivity analysis is useful for measuring the degree of risks and uncertainties related to the CBA results. Sensitivity analysis is a parametric method to determine the extent of changes in the economic indicators [51].

Sensitivity analysis is conducted for the current study for different outcomes, for a varying level of cost and benefit estimates (**Table** *7*). For instance, considerably divergent capital investment cost estimates and fluctuations in demand can affect the price of the sale.

Key risk factors in the sensitivity analysis were identified in accordance with Ref [33]:

i. Cost overrun for capital investment (i.e., 100%, 200% and 400%) and total cost (i.e., 20%, 50% and 70%);
ii. Underachievement of benefit such as price of sale decreased by 10%, 20% and 50%;
iii. A simultaneous increase in cost (i.e., 10%, 20% and 50%) and shortfall in benefit (i.e., 10% and 20%);
iv. Varying discount factors.

Table 7. Sensitivity Analysis of Antibacterial Biocomposite Food Packaging

Scenarios	**NPV (Million AU$)**
100% cost overrun for capital investment	6.37
200% cost overrun for capital investment	5.61
400% cost overrun for capital investment	3.34
20% increase of total cost	5.02
50% increase of total cost	1.48
70% increase of total cost	-0.87
Price of sale decreased by 10%	5.46

Price of sale decreased by 20%	3.55
Price of sale decreased by 50%	-2.21
10% increase of total cost and 10% decrease of total benefit	4.28
20% increase of total cost and 20% decrease of total benefit	1.19
50% increase of total cost and 20% decrease of total benefit	-2.35
NPV at 5% discount rate (BCR)	7.78 (1.62)
NPV at 10% discount rate (BCR)	5.99 (1.61)
NPV at 15% discount rate (BCR)	4.72 (1.59)

The sensitivity analysis showed the project is sensitive to both (a) benefits generation and to (b) cost increases. A 20% decrease of total benefit coupled with a 50% cost increase will produce a negative NPV. The project will not be viable when the price of sale decrease; for instance, a 50% underachievement of total benefit will generate a negative NPV. In addition, the NPV is sensitive to the amount of total cost required. If there is a 70% increase of total cost, the NPV will be negative, and the project will not be viable.

The NPV is fairly attractive even at 400% cost overrun for capital investment which indicates that capital investment does not have any major impact on the viability of the project. The discount rate of 6% is considered as standard for all public sector projects in Australia [52]. A varying level of discount rates between 3% and 10% are applied to assess the sensitivity. Although the NPVs decrease gradually when the discount rates increase, the choice of discount rate has no or little influence on the viability of this investment.

An integral financial analysis during product design is an effective communication tool and evidence of viability that will support coordination mechanisms between government, farmers, manufacturers and consumers. This coordination is often facilitated by the national and state governments in many countries, including Australia, who have made commitment to market development initiatives for environmental friendly packaging using biomass [49]. Clear guidelines and co-operative industrial measures such as the Australian Packaging Covenant also govern the optimization of packaging to achieve resource efficiency and reduction of environmental impact without compromising product quality or safety [50].

4 Conclusions

An assessment of technical and financial viability of an antibacterial biocomposite for food packaging has been conducted. Polylactide was compounded with silver nanoparticles-loaded hemp hurd, and injection molded as a biocomposite. The presence of silver nanoparticles assisted in achieving strong antibacterial activity. The mechanical and thermal properties of the biocomposite compatibilized with GMA preclude the need for major re-engineering of the processing and production of these biocomposites for commercial use, in comparison to traditional rigid plastic packaging. The heavy metal and silver migration from the biocomposites into food simulants tested at standard conditions was observed within the safe limits. Financial assessment of this biocomposite manufacturing for food packaging application was carried out, assuming the project as a small scale industry. The results of cost benefit analysis demonstrated that the project is financially viable. A cost-effective, financially viable, antibacterial biocomposite was produced from biomass-based renewable resource and combined with a biopolymer for safe food packaging. This combination of technical and financial analysis will likely bring greater consumer and industry confidence in biocomposites for rigid food packaging.

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5. CONCLUSIONS AND FUTURE WORK

The overarching goal of a food packaging material is containing food in a cost-effective way that satisfies industry requirements and consumer desires, maintaining food safety, and minimizing its environmental impact. Consequently, the recycling dilemma of traditional petroleum based plastic food packaging is causing the market to shift towards selecting eco-friendly materials, which are also safer for use. Biodegradability/compostability thus materialized as a functional requirement for food packaging, as well as a legislative requirement, and is allowing the food packaging producers to develop biocomposites with biodegradable polymers and natural fibres/fillers, as they allow complete degradation in soil through composting, with negligible toxic or noxious emissions. Hence, combining natural fibres and fillers with biodegradable or compostable polymers offers significant environmental benefits as biocomposites.

To date, numerous research works on biocomposites are available in the literature. The use of hemp hurd (HH) as biobased filler and carrier vehicle for an antibacterial agent with poly(lactic acid) (PLA) as polymer matrix, however, was not studied before and this was the key motivation of this undertaking. In this study, antibacterial activity of HH, its potential to use as carrier vehicle for nanoparticles and structural filler in PLA to form biocomposites were experimentally and analytically investigated. The study was conducted in four phases:

1. Characterisation of HH and investigation of the effect of various factors such as retting process and particle size on antibacterial efficacy
2. Determination of the optimum filler content to obtain the desired physical and mechanical properties of HH filled biocomposite and investigation on the processing, crystallization, and thermo-mechanical response of compatibilized HH/PLA biocomposites
3. Synthesis of silver nanoparticles encapsulated into HH (AgNP-HH) and investigation on processing and properties of antibacterial AgNP-HH/PLA biocomposites
4. Assessment of technical and financial viability of the biocomposites for food packaging application

5.1 Potential Application of Antibacterial Hemp Hurd

HH was claimed to be antibacterial in anecdotal reports, however, it was never systematically investigated. Cannabinoids present in HH as well as the phenolic compounds of lignin possibly provide HH substantial antibacterial property. In this study, the antibacterial activity of HH against *E. coli* was studied. It showed significant antibacterial activity in HH, up to 90% reduction in CFU/mL. Furthermore, the distinctive micro-porous structure and high adsorption capacity of HH offers potential for the application as carrier vehicle for nanoparticles to impose multi-functionality in polymer composites.

5.2 Fabrication of Hemp Hurd/Poly(lactic acid) Biocomposites

Biocomposites produced with bioplastics and natural fillers are gaining more and more acceptance in various applications over the past years because of their biodegradability, low cost, and renewable nature. Interfacial adhesion between natural fibres and matrix is the key issue in terms of overall performance, since it dictates the final properties of the composites. In this study, biomass waste hemp hurd was investigated as a filler to reduce the cost of PLA while preserving the biodegradability, with GMA as an interfacial compatibilizer. The effect of GMA grafted PLA on the mechanical properties and interfacial adhesion of the HH/PLA biocomposites was confirmed to be highly beneficial. Effective interfacial adhesion between the PLA and HH in the composites compatibilized with GMA was confirmed through SEM analysis. An increase of crystallinity of PLA in composites determined through DSC and XRD, confirmed the role of HH as a nucleating agent. The onset of thermal decomposition of the biocomposites obtained through TGA was marginally lower than that of neat PLA. Overall, the biocomposite possesses the potential to be cost-competitive, and be durable in service and biodegradable post-service, hence appropriate for packaging and disposable goods applications.

5.3 Silver Nanoparticles-loaded Hemp Hurd/Poly(lactic Acid) Biocomposites

Silver nanoparticles are well known for their strong antibacterial efficacy towards a wide range of both gram-negative and gram-positive bacteria. However, commercial nanoparticles are often characterized by a broad particle size distribution and are typically agglomerated to sizes of several 100 nm which a great concern for achieving a homogeneous distribution of nanoparticles in the polymer matrix. In this study, the silver based antibacterial agent was synthesized in-house, and precipitated on the HH filler using a proprietary method developed in collaboration with Ecofibre Industries Pty Ltd. AgNPs loading on HH filler was confirmed through SEM imaging and XRD crystallinity analysis. The AgNP-HH was compounded with PLA as an AgNP-HH/GMA/PLA biocomposite is potentially cost-effective, yet retains a majority of tensile mechanical properties of the neat PLA. GMA grafting on to PLA was beneficial for the mechanical properties and interfacial adhesion in the AgNP-HH/GMA/PLA biocomposites. The AgNP-HH and AgNP-HH/GMA/PLA biocomposites demonstrated antibacterial resistance against *E. coli*, showing promise as an antibacterial, biodegradable packaging material. Silver migration to the food simulants determined using ICP-OES was 0.20-3.08 mg/kg, which meets the European Union (EU) legislation (2002/72/EC), substantially lower than the permitted value of 60 mg/kg. However, the role of AgNPs in the elasticity of the HH filler is critical for further understanding the thermal/mechanical mechanisms of the biocomposite, and such an investigation constitutes future work by the author.

5.4 Viability Analysis of the Biocomposite for Food Packaging

Technical and financial viability assessment of the antibacterial biocomposite for food packaging was carried out. The biocomposites were produced with PLA and AgNP-HH via extrusion and injection moulding. Strong antibacterial activity was achieved by introducing AgNPs into hemp hurd. Mechanical and thermal properties of the biocomposite compatibilized with GMA exclude the need for any further re-engineering of the processing and production of these biocomposites for commercial use. The heavy metal and silver migration from the biocomposites into food simulants tested at standard conditions was obtained within the safe limits as prescribed by regulatory authorities. Financial assessment of this biocomposite manufacturing for food packaging application was performed assuming the project as a small scale industry through cost-benefit analysis. The results of CBA demonstrated that a cost-effective antibacterial biocomposite was produced from biomass-based renewable resource and combined with a biopolymer for safe food packaging, which is financially viable. An effective policy by the government and public awareness will obviously lead to improved consumers liking and environmental sustainability.

5.5 Contribution of the study

The findings and results obtained from this study showed that the developed antibacterial biodegradable biocomposite is a promising new material for food packaging. The outcomes of this thesis provide the research community and the food packaging industry with more in-depth understanding on the application of functional biocomposite for safe food packaging application, thus filling the knowledge gap that currently exist in environmental friendly and cost effective biocomposite for food packaging. The experimental data, proposed design parameters, and analysis in this study can be important tools for design engineers permitting safe design and development of homogeneously distributed nanoparticles loaded biocomposite, enabling their increased acceptance and utilisation in the mainstream food packaging application. Upon the widespread acceptance of biodegradable biocomposites in food packaging, it is expected that environmental concern from the current packaging sector can be minimised, dependency on the fossil fuel resource can be reduced, and the landfill needed for the used packaging plastic can be significantly reduced.

Furthermore, the results obtained from the study could create a platform whereupon designers, food scientists and engineers could begin to employ biobased materials in their design solutions. It is believed that by understanding the potential of agricultural by-products like HH as structural filler as well as carrier vehicle for antibacterial agents would emerge to incorporate homogeneously distributed nanoparticles to biocomposites in a more functional and economically viable manner. The financial and sensitivity analysis also provides potential entrepreneurs the degree and magnitude of uncertainties related to the investment to enable better product design.

5.6 Recommendations for Future Work

The following recommendations have been formulated for future investigations.

- Future work may focus on the development of new antibacterial biocomposites to be used in the area where contamination by microorganism is of concern such as medical devices, healthcare products, water purification, hospitals and dental office equipment, food packaging, and household sanitation.
- In this research, no chemical or physical treatment was used on hemp hurd except grafting of GMA; the use of other coupling agents and surface treatment should be considered to improve fibre/polymer interfacial bonding and provide better mechanical and thermal properties of the biocomposites.
- Since the GMA compatibilizer improved the mechanical properties of the biocomposites, further characterizations on this aspect should be done.
- The use of plasticizer on the biocomposites should be investigated to improve processability and pliability of the biocomposites since the brittleness of the biocomposites is a major obstacle for their application in some food packaging.
- The role of AgNPs in the elasticity of the HH filler should be investigated to understand the thermal/mechanical mechanisms of the biocomposite

- Investigation on water vapour, O_2 and CO_2 barrier properties of the biocomposites should be carried out to specify type of food can be packaged.
- Performance, cost and environmental impact comparison on PP, PLA and HH/PLA should be conducted for further understanding the overall value of the material development.

This study provided insightful analysis on the development of an antibacterial biocomposite for rigid food packaging, with acceptable levels of heavy metal migration in food simulants. Its validity should be established with real food systems under real storage and release condition.

APPENDIX A: Statements of Contributions of Co-authors

Appendix A-1: Statements of contribution of co-authors relating to

Khan, B. A, Warner, P and Wang, H. (2014). Antibacterial Properties of Hemp and Other Natural Fibre Plants: A Review. BioResources Vol. 9, Issue 2, pp 3642-3659

11 August 2016

To Whom It May Concern

I, Hao Wang, contributed by project supervision and manuscript editing to the paper/publication entitled

“Antibacterial Properties of Hemp and Other Natural Fibre Plants: A Review”

Undertaken with Belas Ahmed Khan

Student and Co-Author signatures are held at USQ.

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I, Phillip Warner, contributed by project supervision and manuscript editing to the paper/publication entitled

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Appendix A-2: Statements of contribution of co-authors relating to

Khan, B. A, Wang, J., Warner, P and Wang, H. (2015). Antibacterial Properties of Hemp Hurd Powder against *E. coli*. Journal of Applied Polymer Science, Vol. 132, Issue 10

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Appendix A-3: Statements of contribution of co-authors relating to

Khan, B. A, Chevali, V. S., Na, H., Zhu, J., Warner, P and Wang, H. (2015). Processing and properties of antibacterial silver nanoparticle-loaded hemp hurd/poly(lactic acid) biocomposites. Composites Part B, Vol. 100, pp 10-18

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APPENDIX B: Copyright Information

Appendix B-1: Copyright information relating to

Khan, B. A, Warner, P and Wang, H. (2014). Antibacterial Properties of Hemp and Other Natural Fibre Plants: A Review. BioResources Vol. 9, Issue 2, pp 3642-3659

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