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

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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.

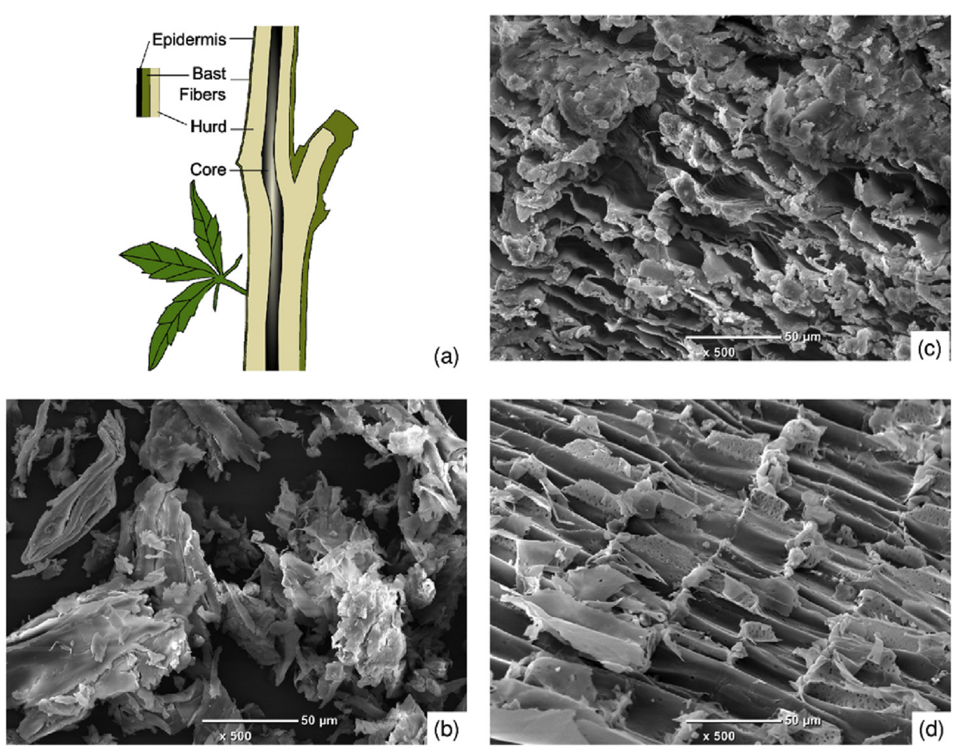

Fig. 1. The morphology of hemp plant and the derivative hemp hurd shown as (a) component of the stem, (b) pulverized as filler, (c) transverse hurd cross section, and (d) longitudinal hurd cross section.