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A comprehensive study on enhanced characteristics of modified polylactic acid based versatile biopolymer

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ABSTRACT

Now a days, polylactic acid (PLA) and its derivatives are receiving significant attention due to its versatile applications. The present study provides a deep insight on major structural and functional properties of novel PLA–HA polymer synthesized by incorporating humic acid (HA) in PLA. Topographical features of both pure and modified PLA have been studied using SEM and AFM to analyze their comparative surface microstructures. Incorporation of HA was found to enhance slightly the thermal stability profile of the polymer. However, reduction of T_g, T_m and degree of crystallinity has also been noticed, which in turn resulted in enhanced ductility and higher elongation at break. Moreover, improvement in radical scavenging properties, total available phenolics (0.075 μmole GAE/g film) and water absorption capacity (90.65%) has been observed which essentially suggested introduction as well as enhancement of several utility features, originally absent in pure PLA. The study thus predicts multifaceted applications of PLA–HA polymer, from industrial packaging to fabrication of biomedical devices depending on its superior characteristics as compared to pure PLA.

1. Introduction

Biopolymers, in last few decades, have achieved much appreciation as an alternative to petrochemical-based plastics because of their unique advantages like biodegradability and origin from renewable feedstocks [1–3]. Among the prevailing biopolymers, polyesters have grabbed prime attention of many scientists due to their diverse applicability, facile biodegradability and hydrolysability of ester bonds into non-toxic matters [4,5]. PLA (polylactic acid), PCL (poly(e-caprolactone)) and PHA (polyhydroxyalkanoate) for instance are some of them.

Polylactic acid (PLA) being a thermoplastic polyester are innately biocompatible, bioresorbable and biodegradable in nature. It has the potentiality to be used in the field of pharmacology and textile industries. Moreover, its monomer synthesis using suitable microorganisms and renewable resources reduced the apprehension of global warming to some extent [5]. However, PLA has some inherent disadvantages like; its surface does not have any cell recognition site which is unfavorable for cell growth in tissue engineering. Additionally, being brittle in nature, its application as packaging material is also reduced. Therefore, its functional modifications seemed to be of primary importance.

In order to counter this task, bulk and surface modifications of PLA using chemical or synthetic agents through copolymerization, blending, crosslinking, incorporation of protein and antioxidants, plant oil, etc. has been tried

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[6–10]. These processes yield polymers with enhanced functional properties through the modification of native polymeric chains, where the functionalities depend on the nature of additives used.

However, the use of such foreign materials is increasingly questioned by consumers due to their health risks and toxicity [11]. Another note worthy aspect of these modifications is that the inherent distinctive properties of the polymer should not get changed drastically. Hence, scientists have endeavored to use natural sources to modify native PLA to improvise its functional properties. Apart from enhancing the bulk properties of a polymer, natural phenolic compounds like hydroxy and polyhydroxy derivates of cinnamic acids such as caffeic, coumaric, and ferulic acids have been reported to impart their additional functional properties like enhanced water absorption, free radical scavenging etc. Their reactivity against this unpaired electron species is dependent on both the number of phenolic groups present in the molecule and the substitution pattern in the aromatic ring [12,13].

Humic acid (HA), a natural phenolic compound, is ubiquitously present in soil, aquatic bodies, peat, coal etc. Owing to its abundant availability, easy extraction process and versatile applicability, it is considered to be a low cost commercially valuable compound for various industrial applications [12]. It is neither a single acid, nor does it have a unique molecular structure. Rather, it is a complex mixture of many different acids containing carboxylic, phenolic, carbonyl, hydroxyl, amine, amide, aliphatic moieties etc. attached together as a single molecule with the help of hydrogen, ester, ether and other covalent bonds. Studies on the chemical characterization of humic acid indicate that the amount of different functional groups vary significantly between humic substances of different origin. The precise properties and structure of a given humic acid depends on its source and the specific conditions of extraction. The tentative structure of humic acid has been shown in Fig. 1. Moreover, along with the versatile functional group content, its antioxidant, anti inflammatory and other therapeutic benefits, made scientists more focused to explore its other nonconventional applications like crosslinking during polymerization, improving biological properties of polymer, etc. [14].

As mentioned earlier, modification of PLA in order to improve its functional properties is the main focus of current research. In this context, HA, a complex polyphenol containing wide range of functional groups has recently been exploited as an active agent to impart crosslinking as well as to incorporate reactive groups to the PLA chain [15]. HA has proved its applicability in the domain of biopolymer production, moreover, being the principle component of humic substances, i.e., of biological origin, its use can be considered to be both environmentally and biologically safe.

The present article focuses on advanced characterization of eco-friendly bioactive PLA film produced through incorporation of HA, a natural antioxidant as well as functional modifier. To evaluate the potentiality of the developed film for different industrial and biomedical applications, the microstructural, thermal, mechanical, antioxidant and water absorption capacity of the film were also studied.

2. Experiment

2.1. Polymer synthesis

PLA was synthesized from purified L-lactic acid, obtained from the fermentation of *Zizyphus oenophlia* using *Lactobacillus amylophilus* GV6. Substrate: media ratio of 3:2, inoculum volume 3% and pH 6.5 was the optimized condition. Fermentation under the above mentioned condition has resulted in 95.09% conversion [15,16]. Humic

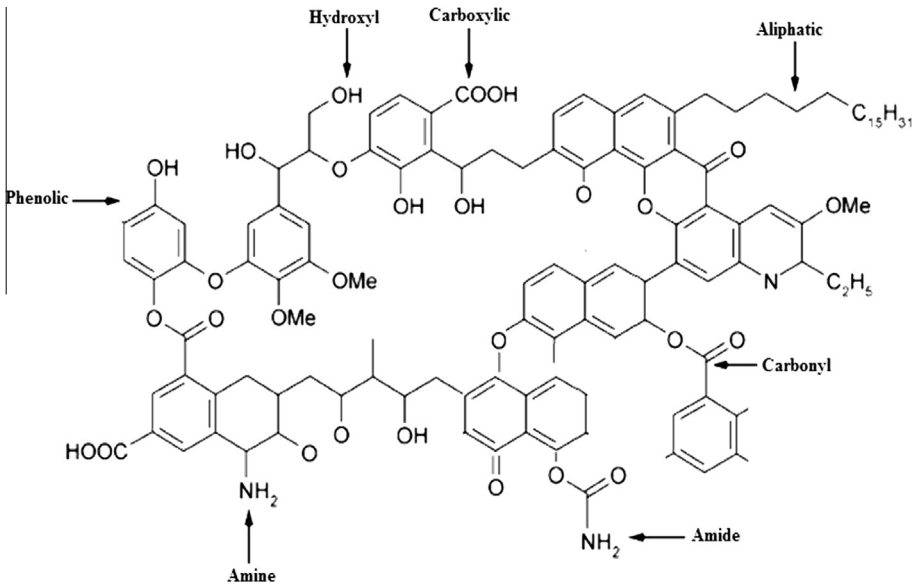

Fig. 1. Probable structure of humic acid.