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BIOENERGIA

PROGRAMA INTEGRADO (UNESP, USP E UNICAMP) DE PÓS-GRADUAÇÃO EM BIOENERGIA

CHEMICAL COMPOSITION AND PHYSICOCHEMICAL CHARACTERIZATION OF FRUIT WASTE, AND THE USE OF MACROMOLECULES IN BIOPLASTIC AND BIOCOMPOSITE PRODUCTION

ROGERIO MARTINS VIEIRA

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Tese apresentada ao Instituto de Pesquisa em Bioenergia de Rio Claro, Universidade Estadual Paulista, como parte dos requisitos para obtenção do título de Doutor em Ciências.

Orientador: Dr. Michel Brienzo
Coorientador: Dr. Nelson Ramos Stradiotto

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I dedicate this work to my family and friends, whose support, love, and companionship were essential for making this dream come true, especially to my late grandfather Rogério Martins.

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“Somos o que fazemos, mas somos, principalmente, o que fazemos para mudar o que somos.”

(Eduardo Galeano, 1989)

ABSTRACT

Waste generation from fruit production is a serious environmental problem due to challenges related to its final disposal, despite being a valuable feedstock for numerous value-added applications. This study aimed to comprehensively characterize the physicochemical properties of three major fruit residues from São Paulo State, Brazil: banana pseudostem, orange bagasse, and guava seed, and to explore the application of modified lignin in the production of bioplastics and biocomposites. The biomasses were analyzed for their chemical composition, optimal extractive removal time, particle size, structural properties, and the potential use of macromolecules. Extractives were removed from 1 g of each material using ethanol and water separately for 4, 8, 12, and 16 hours, as well as sequentially with ethanol followed by water for 8 hours each as a control. Chemical composition was determined based on the contents of cellulose, hemicellulose, lignin, extractives, and ash using acid hydrolysis with 72% sulfuric acid (w/w). The results indicated that 4-hour extraction was sufficient for all materials, and the biomasses exhibited distinct compositions. Guava seed had the highest lignin content, at 41.66% (dry basis); banana pseudostem had 33.97% cellulose; and orange bagasse presented a high extractive content of 60.78%. All biomasses showed a total component content greater than 92%, supporting the applicability of these chemical characterization methods to fruit residues. For particle size evaluation, five granulometries were randomly selected (850, 600, 425, 250, and 106 μm) and analyzed in natura, extractive-free, and extractive/pectin-free forms using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The effect of particle size on extractive content was most pronounced when comparing the 850 μm and 106 μm fractions, with variations of 8.40% for orange bagasse and 44.72% for banana pseudostem. Pectin removal also showed a significant influence between the 850 μm and 425 μm particles, with differences of 24.14% and 25.86%, respectively. FTIR spectra revealed increased band intensity after particle size reduction. SEM images showed characteristic lignocellulosic surfaces and some structural modifications after extractive removal. XRD analysis indicated a strong influence of granulometry on the crystallinity of all samples. As a valorization strategy, lignin was extracted from banana pseudostem using the organosolv method, modified via esterification with maleic anhydride, characterized, and used as an additive in chitosan-based films produced by the casting method with 2 and 5 wt% of esterified lignin, and in polylactic acid (PLA) matrices via melt compounding followed by compression molding with 5 and 10 wt% of esterified lignin. Lignin addition mainly resulted in improved hydrophobicity, with a 14.4% reduction in water vapor permeability for chitosan-based films; complete UV-blocking efficiency in all lignin-PLA composites; and increased antioxidant activity in both materials compared to the controls. These results demonstrate that the use of modified lignin in bioplastics and biocomposites offers a promising pathway for developing advanced and sustainable materials, while contributing to the valorization of fruit production waste.

Keywords: Bioplastic; Biocomposite; Banana pseudostem; Orange bagasse; Guava seed.

RESUMO

A disposição final dos resíduos gerados na produção de frutas é um sério problema ambiental, os quais são matéria-prima notável para inúmeras aplicações de valor agregado. Este estudo teve como objetivo a completa caracterização físico-química de três principais resíduos de frutas produzidos no estado de São Paulo (Brasil), sendo o pseudocaule da bananeira, o bagaço de laranja e a semente de goiaba, bem como o uso da lignina modificada na produção de bioplásticos e biocompósitos. As biomassas foram analisadas com base na sua composição química, tempo ideal de remoção de extrativos, tamanho de partícula, propriedades estruturais e potencial uso de macromoléculas. Os extrativos foram removidos a partir de 1 g de material, utilizando separadamente etanol e água como solvente por 4, 8, 12 e 16 horas cada, e a sequência etanol-água por 8 horas cada foi utilizada como controle. A composição química foi determinada por hidrólise ácida com H_2SO_4 72% (m/m). Os resultados mostraram que 4 h de extração foram suficientes para todos os materiais com ambos os solventes, e foi observada uma composição variada entre as biomassas. A semente de goiaba apresentou o maior teor de lignina, 41,66% (em base de massa seca), o pseudocaule da bananeira apresentou 33,97% de celulose e o bagaço de laranja apresentou alto teor de extrativos, de 60,78%. Todas as biomassas obtiveram a soma de componentes superior a 92%, o que sugere a aplicabilidade de tais métodos de caracterização química para resíduos de frutas. Para a avaliação granulométrica, cinco granulometrias diferentes foram selecionadas aleatoriamente, 850, 600, 425, 250 e 106 µm, e analisadas na sua forma *in natura*, livre de extrativos e livre de extrativos/pectina por espectroscopia no infravermelho com transformada de Fourier (FTIR), microscopia eletrônica de varredura (MEV) e difração de raios-X (XRD). De acordo com os resultados, foi observado que o tamanho de partícula influenciou no teor de extrativos principalmente entre as granulometrias de 850 e 106 µm, com variações de 8,40% (em base de massa seca) para bagaço de laranja e 44,72% para pseudocaule de bananeira. Em relação à remoção de pectina, houve influência significativa entre partículas de 850 e 425 µm, de 24,14% e 25,86%, respectivamente. Os espectros de FTIR mostraram um aumento na intensidade das bandas após a redução do tamanho das partículas, enquanto as imagens MEV mostraram superfícies típicas de materiais lignocelulósicos e algumas modificações na estrutura da fibra após a remoção dos extrativos. A partir dos dados de XRD, foi detectada uma influência significativa da granulometria na cristalinidade de todas as amostras. Como uma abordagem de valorização, a lignina foi extraída do pseudocaule da bananeira pelo método organosolv, modificada através da reação de esterificação usando anidrido maleico, caracterizada e usada como aditivo em filmes à base de quitosana produzidos por casting a 2 e 5% (m/m) de lignina esterificada. Foi incorporada também a matrizes de ácido polilático (PLA) via melt-compounding seguido de moldagem por compressão, usando 5 e 10% (m/m) de lignina esterificada. A adição de lignina resultou principalmente em melhora da hidrofobicidade, com uma redução de 14,4% na permeabilidade ao vapor de água para o filme à base de quitosana; eficiência completa de bloqueio da luz UV para todos os compósitos de lignina-PLA; e aumento da atividade antioxidante para ambos os materiais em comparação com os controles. Esses resultados mostraram que o uso de lignina modificada para produzir bioplásticos e biocompósitos surge como uma alternativa para o desenvolvimento de materiais avançados e sustentáveis, bem como a valorização de resíduos da produção de frutas.

Palavras-chave: Bioplástico; Biocompósito; Pseudocaule de bananeira; Bagaço de laranja; Semente de goiaba.

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GENERAL INTRODUCTION

The human diet comprises a wide variety of foods, with fruit consumption being particularly important due to its nutritional benefits. Brazil is the third-largest fruit producer in the world, with a total output of approximately 40 million tons in 2021 (FAO, 2023). Among the most widely cultivated fruits globally are orange (*Citrus sinensis*), banana (*Musa* spp.), and guava (*Psidium guajava*), which are consumed both fresh and processed by the food industry (PEREIRA et al., 2022). However, this high level of production generates large volumes of agro-industrial waste, which, if not properly managed, can lead to environmental issues such as soil and water contamination. On the other hand, these residues are rich in lignocellulosic biomass and represent a valuable resource for the production of high-value products within the bioenergy and biorefinery sectors.

Lignocellulosic biomass primarily consists of cellulose, hemicellulose, and lignin, along with smaller quantities of pectin, extractives, and ash. The specific composition of each biomass type determines its potential applications, which can be assessed through qualitative and quantitative analytical techniques. Established methods, such as those developed for wood and sugarcane bagasse, important raw materials in the paper and bioethanol industries, are commonly used for compositional analysis (SLUITER et al., 2008). Nevertheless, there is no universal method for evaluating the physicochemical properties of all types of fruit biomass. Consequently, traditional protocols often require adaptation. Challenges in the analysis include sample preparation steps, such as removing extractives, adjusting for moisture content, and reporting results as means with standard deviations based on independent replicates (VIEIRA et al., 2023). Notably, fruit residues typically present high moisture and extractives content, especially those derived from industrial processes, which distinguishes them from materials like sugarcane bagasse.

Comprehensive chemical, physical, and structural characterization is essential for assessing the potential applications of lignocellulosic biomass. This is especially important considering the wide availability, low cost, and environmental benefits of these materials. A broad range of applications has emerged for fruit biomass, including the extraction of bioactive compounds, development of nanocomposites, and production of biofuels, biogas, and bioplastics (DE FREITAS; BRIENZO, 2023; FREIRE et al., 2023; MACEDO et al., 2022).

Particle size is a critical factor influencing the compositional and structural analysis of biomass. It directly affects surface area, heat transfer, and the bioaccessibility of lignocellulosic components, all of which are important for biomass conversion processes (FERNANDES et al., 2020). Previous studies have shown that reducing particle size can enhance the efficiency of pretreatment steps, leading to improved cellulose accessibility and higher glucose yields (DEB et al., 2016). Furthermore, common physicochemical characterization techniques, such as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM), can yield higher quality results when optimized particle size is used. Grinding is often necessary for non-fibrous fruit residues, which lack the structural consistency found in sugarcane bagasse or wood.

The production of bioplastics from macromolecules extracted from fruit residues has gained interest, particularly when these are blended with other biopolymers such as chitosan and polylactic acid (PLA) (ODILI et al., 2025; PHAM et al., 2024). Lignin, in particular, has shown promise as an additive due to its antioxidant and UV-blocking properties, as well as its ability to enhance the hydrophobicity of bioplastic matrices (SONG et al., 2021). However, the inherent insolubility of lignin in most organic solvents and its poor compatibility with non-polar polymers present significant challenges. These limitations can be overcome through chemical modification techniques that enhance lignin's processability and compatibility with polymer matrices, thereby contributing to the valorization of both lignin and agro-industrial waste (YAN et al., 2022).

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GENERAL CONCLUSION

In recent years, numerous strategies have been developed to promote the sustainable utilization of food waste, particularly within the growing bioenergy and biorefinery industries. Among these, fruit waste has gained prominence as a promising feedstock due to its biodegradability, low cost, and wide availability, especially in tropical countries like Brazil.

Compositional analysis plays a critical role in evaluating the potential applications of fruit waste, as its chemical profile varies considerably between species and among different parts of the same plant. Although cellulose and hemicellulose are not typically solubilized in ethanol and water under the extraction conditions used for removing extractives, significant solubilization of monomeric sugars was observed in orange bagasse after prolonged extraction periods. This finding may affect the accuracy of its absolute compositional analysis. Nonetheless, conventional chemical characterization methods, commonly applied to sugarcane bagasse and wood, proved effective for fruit biomass as well. However, due to observed interferences, pectin requires specific attention in the case of orange bagasse, necessitating its separate extraction and quantification prior to broader compositional analysis. Additionally, FTIR spectroscopy enabled qualitative assessment of extractives, a rarely explored aspect in current literature.

Particle size is another important factor influencing the efficiency of lignocellulosic biomass conversion. In this study, its effect was particularly significant over a wide particle size range (850 μm vs. 106 μm), suggesting that for more homogeneous materials, extensive grinding may be unnecessary. This has favorable implications for process efficiency, logistics, and cost reduction at industrial scale. Structural characterization further revealed that the removal of extractives and pectin affected the crystalline-to-amorphous ratio within the biomass.

The esterification of lignin extracted from banana pseudostem using maleic anhydride was successfully confirmed by changes in molecular weight, FTIR, and ^{1}H NMR data. The incorporation of esterified lignin into chitosan-based films resulted in significant improvements in UV-blocking performance, reaching up to 100% efficiency, and enhanced hydrophobicity, as indicated by a 14.4% reduction in water vapor permeability. Similar enhancements were observed in PLA-lignin composites, including an 84.9% increase in antioxidant activity compared to neat PLA. However, a decrease in tensile strength was noted, likely due to poor dispersion and the loss of functional groups during chemical modification.

Overall, this study provided a detailed physicochemical characterization of three fruit waste types commonly found in the Brazilian market, offering valuable data to support their sustainable valorization. The observed enhancements in chitosan-based films through lignin incorporation highlight their potential as effective materials for food packaging, contributing to extended shelf life. Similarly, the application of banana pseudostem lignin as a green additive in PLA composites represents a promising sustainable strategy for agricultural use, such as in mulching films. This approach adds value to fruit production residues while mitigating the environmental impacts associated with their disposal.