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Development and characterization of gelatinized starch doped microcellulose paper from tender coconut (*Cocos nucifera* L.) husk

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ABSTRACT

Cellulose-starch based composite papers can be used as packaging materials due to their biodegradable and renewable properties. In this study, biodegradable composite paper were developed from tender coconut husk with starch as an additive. Potato and corn starch were added to the matrix at a ratio of 5%, 10% and 15% and were evaluated for the mechanical, physical, and structural properties as well as the biodegradability of the biocomposite paper. The tensile strength and the elongation percentage of the developed biocomposite paper varied from 12.45 ± 1.69 MPa to 9.52 ± 4.30 MPa and $9.76 \pm 0.99\%$ to $15.52 \pm 3.27\%$ respectively. The results indicate a decreasing trend in tensile strength with increasing starch concentration, attributed to reduced hydrogen bonding density. Moisture content analysis shows no significant difference between starch types. The composition of the paper was analyzed using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The outcomes demonstrated the existence of robust interactions between the hydroxyl groups of starch and cellulose of coconut husk matrix. Moreover, the material showed a degradation rate of approximately 70% within a 20-day period, demonstrating its suitability for the production of biodegradable material. This study suggests that tender coconut husk is a promising material for the production of paper intended for packaging applications.

1. Introduction

Plastic pollution is pervasive in both land-based and aquatic ecosystems, posing a significant threat to all living organisms. The indiscriminate use, insufficient recycling, and landfill deposits of plastic are contributing to an unprecedented rise in plastic production and accumulation in the natural environment. Microscopic plastic particles, easily consumed by organisms, can accumulate and transfer up the food chain, posing a significant threat to both animals and humans alike (Khanashyam et al., 2023). As of 2019, worldwide plastic production reached 370 million tons, of which only 9% was recycled, 12% was incinerated, and the remainder ended up in the environment or landfills

(Kumar et al., 2021). Therefore, the need for alternative materials to substitute synthetic plastics has become more crucial, given the environmental concerns and the growing public awareness. Moreover, sustainability has become a crucial topic in recent years, and the packaging industry is no exception. The growing apprehension among consumers about the ecological repercussions of packaging materials has resulted in an upsurge in the desire for environmentally friendly substitutes (Lindh et al., 2016). The packaging industry is one of the largest contributors to global plastic waste (Ncube et al., 2020), and finding eco-friendly alternatives is crucial to reduce the environmental impact of packaging. There is a substantial need for disposable cutlery, exemplified by the annual consumption of 40 billion plastic cutlery items in the United

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States and the disposal of 120 billion plastic cutlery pieces in India each year (Boro et al., 2020). The worldwide demand amounts to 640 billion annually, and as of 2017, the global plastic cutlery market was valued at US\$ 2.62 billion, as reported by the Digital Journal. Projections indicate an expected increase to approximately US\$ 3 billion by the year 2025 (Boro et al., 2020). The Sustainable Development Goals (SDGs), launched by the United Nations in 2015, provide a framework to address global challenges. Biodegradable packaging materials have the potential to contribute to achieving multiple SDGs. They can support Goal 12 by reducing waste and pollution, Goal 13 by lowering the carbon footprint of packaging, and Goal 14 by mitigating plastic waste in oceans and protecting marine ecosystems.

The coconut tree is a significant plant worldwide, serving as a source of nourishment, energy, and fiber for billions of individuals, particularly in tropical and subtropical areas. One of its valuable products is the clear, nutritious liquid found inside the coconut, known as coconut water. In recent years, the rising popularity of consuming young coconut water has led to an expansion of the coconut water market in many countries. However, this increased consumption has also resulted in the generation of more by-products, such as coconut husks, which make up approximately 60–65% of the fruit's weight (Pandiselvam et al., 2021). Unfortunately, these husks are often discarded on embankments and left to degrade in the open environment, a process that can take up to a decade. Consequently, the consumption of tender nut water results in the creation and accumulation of bio-waste, contributing to soil contamination. In the realm of sustainable packaging, the exploration of biodegradable materials has gained prominence, steering attention towards coconut husk-derived coir fibers. Extensive research has been conducted to integrate coir fibers into biocomposites, showcasing their potential as reinforcing agents. Biocomposites, utilizing starch/EVOH/Glycerol blends as matrices, revealed notable improvements in tensile modulus with varying coir fiber content (Rosa et al., 2009). Surface treatment further enhanced interfacial bonding, augmenting mechanical properties (Nam et al., 2011). Beyond biocomposites, coir fibers found applications in paper making and cardboard production, influencing tensile and tear strength based on fiber content, beating time, and soaking conditions (Othman et al., 2013; Hamouda, 2021). Moreover, innovative uses include binderless fiberboard from unripe coconut husk and coir fibers as cushioning materials, showcasing promise in diverse packaging scenarios (Hamouda, 2021). These endeavors mark a significant stride toward environmentally friendly and sustainable packaging solutions, addressing the contemporary challenges associated with conventional materials like plastics. Hence, there is an imperative to explore innovative approaches for utilizing tender coconut husks, especially with a focus on value addition.

The chemical composition of tender coconut husk indicates that cellulose fibers comprise around 44–45% of its composition, along with hemicellulose (7–8%), lignin (approximately 37%), pectin (4–4.5%), and waxy substances (3–3.5%) (Pandiselvam et al., 2023). The tender coconut husk, particularly the white fibers obtained from young coconuts, have a notable cellulose content, and this natural fiber, often overlooked and treated as waste, stands out for its high tensile strength, hightoughness and durability presenting a distinct advantage over other agricultural biomass (Silva et al., 2000). In India, where coconut production reaches about 22.96 billion nuts annually (Narmadha, 2022), and despite this abundance, coconut husk fibers remain underutilized. Recognizing the untapped potential of these fibers could not only contribute to sustainable practices but also pave the way for innovative applications in bioplastics, aligning with the global trend toward environmentally friendly materials. The high concentration of lignin in tender coconut husk causes it to decompose slowly, which leads to environmental pollution. To prevent this, it is essential to convert these cellulosic fibers into useful products, such as biodegradable packaging materials, to reduce environmental pollution. Lately, there has been significant focus on developing completely biodegradable blends using natural polymers and their derivatives such as cellulose (Ferreira et al.,

2018), starch (Jiang et al., 2020), chitin and chitosan (Yu et al., 2020), protein (Nazmi et al., 2020) etc. for packaging applications. Cellulose and its derivatives, including carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), and bacterial cellulose (BC), exhibit favorable characteristics for film formation. These properties lead to the production of biodegradable, non-toxic, and transparent films with exceptional mechanical, thermal, and barrier properties against oxygen and oil (Amin et al., 2021). In pursuit of maintaining biodegradability, reducing costs, and enhancing the mechanical durability of end products, researchers have conducted experiments on blending cellulose with plasticized starch. In a study, Wu et al. (2009) created a composite membranes for fresh food packaging by blending cellulose, starch, and lignin in a specific solvent. The experimental findings indicated that the proportions of these components affected the mechanical properties of the films, which demonstrated excellent mechanical strength and transparency. While the reinforcing capabilities of cellulose fibers in plasticized starch are widely recognized (Ruhul Amin et al. (2019), Zeleke (2023), limited attention has been given to investigating the toughening effect of plasticized starch on cellulose Wu et al., (2009). The rationale for selecting potato and corn starch is rooted in their prevalence and relevance as biodegradable materials for producing films used in food packaging. The study seeks to provide a comprehensive understanding of the structural differences and unique characteristics of potato and corn starch. Corn starch, being the predominant global starch source (constituting around 65% of total starch production), has emerged as a key material for biodegradable polymers (Luchese et al., 2018). In parallel, potato starch, while contributing a smaller share, is strategically chosen for its unique properties. Study by de Azevedo et al. (2020) have shown that bioplastics made from corn starch exhibited superior physical, mechanical, and thermal properties, as well as better optical quality, compared to those based on potato starch whereas, thermal resistance was higher in corn starch-based bioplastics. However, biodegradation was faster in potato starch-based bioplastics (5 days) compared to corn starch-based ones (almost 40 days). Materials derived from cellulose are widely available, cost-effective, and readily accessible from sustainable natural sources. Additionally, they offer advantages such as comparatively lower density, higher specific stiffness, and strength, which facilitate the creation of low-density composites with greater filler content (Ortega-Toro et al., 2017). Coconut husk based biodegradable packaging materials offer a sustainable solution as it can contribute to the circular economy by reducing waste and utilizes a byproduct of the coconut industry. This can help create a more sustainable and efficient economy that reduces the environmental impact of packaging. To the best of our understanding, no research has been conducted on manufacturing biodegradable paper using tender coconut husk. Hence, the purpose of this investigation was to create and examine a biodegradable paper made from tender coconut husk.

2. Materials

2.1. Raw materials

Tender coconut husk was collected from Street Vendors, Thiruvananthapuram, India and NaOH was procured from M/S Molychem, Mumbai, Maharashtra, India. Corn and potato starch was obtained from M/S Stanes, Thiruvananthapuram, India.

2.2. Experimental method

The process flow for preparing packaging material from tender coconut husk involved preprocessing, alkaline pulping and drying of pulp. Initially, tender coconuts husk (obtained from 6 to 7 months matured coconut) were mechanically shredded using a hammer mill (developed by CSIR-National Institute for Interdisciplinary Science and Technology (NIIST), Trivandrum) at 1800 rpm. The resulting pulverized husk was subjected to an alkaline treatment using 20% NaOH at 110°C for 3.5 h to

remove unwanted substances such as gums, hemicelluloses, lignin, wax, and oils from the fibers. The mixture was then washed with tap water until the pH of the draining water reached 7 and the pulp was allowed to drain for 30 minutes. The drained pulp was further ground in a high-capacity blender (M/S Parason, Trivandrum, India) at 25,000 RPM to ensure uniform fiber consistency. In the next step, potato and corn starch were converted into a solution by modifying the process described by Bertuzzi et al. (2012) and Niu et al. (2021), and the starch solutions were mixed with the prepared pulp in pre-defined ratios (Table 1) obtained from preliminary studies. The resulting pulp-starch mixture was transferred into a porous stainless-steel tray measuring 800 × 400 × 25 mm and covered with muslin cloth. The tray was then dried at 60°C for 6 hours to obtain the final packaging material. A flow diagram of the process is given in Fig. 1.

2.3. Characterization of developed biodegradable packaging material

2.3.1. Mechanical properties

The tensile strength of 15 cm × 2 cm samples was assessed using a Tinius Olsen H5 Ks with a 5 KN load cell. Each sample was replicated five times, and the graph obtained was used to determine the tensile strength and elongation at break. A Digital Vernier calliper (Generic 150 mm/6 Inch) were used to find the film thickness. The thickness was measured at five different locations on each sample, and the mean thickness was calculated with an accuracy of ± 0.2 mm.

2.3.2. Moisture content

The moisture content was analyzed by following AACC method No. 44–15 A (AACC 2000).

2.3.3. Contact angle

The surface hydrophobicity was measured by using an optical contact angle measurement device (OCA 15EC, dataphysics, Germany) by sessile drop technique and data were analyzed by the software OCA 20.

2.3.4. X-ray diffraction (XRD)

The crystallinity and structural properties of the samples were examined using a powder X-ray diffractometer (Malvern PANalytical PC controlled X-Ray Diffractometer, United Kingdom) following Skendi et al. (2022) methodology. A scan speed of 50/min was implemented between 50 and 900, using Ni-filtered CuK radiation, at a voltage of 40 KV and an electrical current of 40 mA. The crystallinity index (CI) was determined using the approach proposed by Yao et al. (2020). Peaks in the data were separated using Origin pro software (SRO-9.8) to analyze the information.

2.3.5. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra were analyzed to observe alterations in different peaks resulting from the use of various combinations of biodegradable pulp. The spectra were obtained using a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory, ranging from 4000 cm⁻¹ to 400 cm⁻¹. The spectrophotometer software (OPUS) was used to analyze the FTIR spectra.

Table 1

Composition of the prepared biodegradable pulp.

| Sl No | Components | Composition 1 | Composition 2 | Composition 3 |
|-------|----------------------------------|---------------|---------------|---------------|
| 1 | Tender coconut | Control | Control | control |
| 2 | Tender coconut and corn starch | CS1 95:5 | CS2 90:10 | CS3 85:15 |
| 3 | Tender coconut and potato starch | PS1 95:5 | PS2 90:10 | PS3 85:15 |

2.3.6. Scanning electron microscopy

The prepared biodegradable material was subjected to morphological analysis using a scanning electron microscope (EVO-60, ZEISS, Germany). The dry samples were freeze-dried to eliminate any remaining moisture and coated with gold (2 m bar) using sputtering before being placed on circular aluminum stubs for examination. The sample was then observed at 15 kV and a vacuum of 9.75×10^{-5} torr.

2.3.7. Soil burial test

A soil burial experiment was conducted at the laboratory scale to investigate the biodegradability of the samples. From each sample, specimens of specific sizes were prepared and packed in PVC fiber net which is then placed plastic containers with small holes punctured at the bottom and sides were filled with moist soil to improve air and water circulation. A total of 3 composite sheet samples (control and 15% corn and potato starch infused samples) were buried and periodically removed to monitor visible changes.

2.4. Statistical analysis

The experiments were conducted three times to ensure accuracy. The data were analyzed through Analysis of Variance (ANOVA) using IBM Corp. SPSS statistical software package version 22 (Armonk, NY, USA). Duncan's Multiple Range Test was utilized to perform multiple comparisons among the mean values at a significance level of 0.05.

3. Results and discussion

3.1. Mechanical properties

The mechanical properties of cellulose-starch composite paper play a vital role in determining their effectiveness as packaging materials. The tensile strength and elongation at break of the paper are crucial in ensuring its ability to endure stress and deformation during packaging and transportation. These properties are crucial to ensure that the packaging material can protect its contents from external factors such as mechanical stress, impact, and punctures. The tensile strength and elongation of the developed paper is presented in Table 2. The tensile strength of the paper varied from 12.45 ± 1.69 Mpa for 10% corn starch (CS2) to 9.52 ± 4.30 Mpa for 15% corn starch (CS3) incorporated samples. Though variation is not significant, the tensile strength showed a decreasing trend with respect to the increasing starch concentration in the paper matrix. This is because the addition of excessive amounts of starch in bio-composite paper can result in a reduction of the density of hydrogen bonding, leading to a consequent decrease in their tensile strength (Steven et al., 2020). Rosa et al. (2009) observed a similar trend while assessing the impact of different fiber loadings on the ultimate mechanical properties of the prepared starch/ethylene vinyl alcohol (EVOH)/glycerol composite blends matrix, reinforced with varying coir fiber content. The observed decrease in both tensile strength and tensile strain as fibers were introduced to the matrix were attributed to the diminished ductile behavior of the matrix resulting from the incorporation of coir fibers. However, the addition of starch in the manufacturing process of bio-composite paper can prevent the formation of cavities, which may explain the slightly higher values of tensile strength observed for the developed paper as compared to control. Wu et al. (2009) studied the mechanical properties of composite (Cellulose: starch = 85:15) and reported a higher tensile strength and percentage elongation of 28.9 ± 1.8 Mpa and $65.6 \pm 2.8\%$ respectively. The elongation at break of the biocomposite film containing corn starch exhibited no significant difference. However, a significant difference between the treatments ($p < 0.05$) was observed for potato starch incorporated paper and the elongation at break was found to be depended on the starch concentration. The elongation at break varied between $9.76 \pm 0.99\%$ for 10% potato starch incorporated samples (PS2) to 15.52 ± 3.27 for 15% potato starch incorporated samples (PS3).

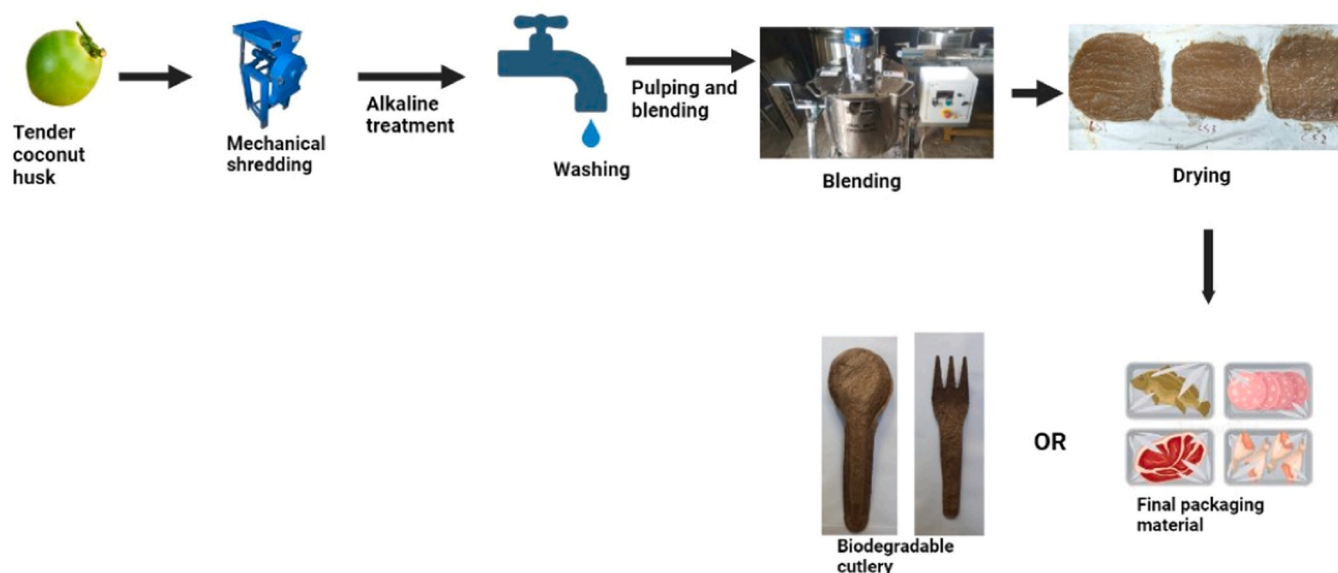


Fig. 1. Schematic diagram showing the preparation of coconut husk-based starch doped cellulose composite paper.

Table 2

The tensile strength, elongation (%) and thickness of the developed biodegradable paper.

| Sample code | Tensile strength (Mpa) | Elongation (%) | Thickness (mm) |
|-------------|---------------------------|---------------------------|--------------------------|
| CS1 | 11.06 ± 1.53 ^a | 10.77 ± 2.07 ^a | 0.92 ± 0.15 ^a |
| CS2 | 12.45 ± 1.69 ^a | 12.67 ± 4.46 ^a | 1.23 ± 0.05 ^a |
| CS3 | 9.52 ± 4.30 ^a | 11.72 ± 1.86 ^a | 1.15 ± 0.06 ^a |
| PS1 | 11.96 ± 1.98 ^a | 11.12 ± 6.33 ^a | 1.35 ± 0.10 ^a |
| PS2 | 10.34 ± 2.60 ^a | 9.76 ± 0.99 ^b | 1.37 ± 0.05 ^a |
| PS3 | 9.90 ± 0.88 ^a | 15.52 ± 3.27 ^b | 1.05 ± 0.06 ^a |
| Control | 10.45 ± 0.71 ^a | 10.85 ± 1.62 ^a | 1.72 ± 0.10 ^b |

Results are presented as mean ± standard deviation of five replicates. Values with same letters are not significantly different at 5% level.

The thickness of cellulose-starch based biocomposite paper is an important factor to be considered during designing of the packaging material as it can affect their mechanical strength, barrier properties, optical properties, and biodegradability. Thicker paper may have higher tensile strength and better barrier properties, while thinner paper may have better flexibility and folding endurance (Bertuzzi et al., 2012). Moreover, thicker paper degrade slower due to reduced surface area and limited access to biodegrading agents (Briassoulis, 2006). Thus, paper thickness is a crucial factor to consider when designing biocomposite paper for specific applications. The thickness of the developed samples varied from 0.92 ± 0.15 mm to 1.72 ± 0.10 mm. There was no significant variation observed in the thickness of the paper concerning the type or concentration of starch used. However, the developed packaging material had a significantly lower thickness ($p < 0.05$) as compared to the control samples. A similar thickness of 1.186 mm were reported by Othman et al. (2013) for a 85% coconut fibers and 15% newspaper blend.

3.2. Moisture content and contact angle

In general, the quality of packaging materials, including their ability to withstand compression when stacked, maintain their shape, resist tearing when folded, and withstand tension, is greatly impacted by the amount of moisture present in the materials (Rhim, 2010). The level of moisture in plant materials is a crucial aspect as water has a plasticizing effect. The moisture content of the initial pulp and the final moisture of the developed biodegradable sheets are shown in Table 3. Though the

Table 3

The thickness, moisture content, and contact angle of the biodegradable composite paper.

| Sample Code | Moisture Content of Pulp (%w.b.) | Moisture Content of Sheet (%w.b.) | Contact angle (°) |
|-------------|----------------------------------|-----------------------------------|---------------------------|
| Control | 95.35 ± 0.93 ^a | 9.50 ± 0.30 ^a | 62.95 ± 3.75 ^a |
| CS1 | 95.64 ± 0.46 ^a | 10.20 ± 0.17 ^a | 68.9 ± 2.40 ^b |
| CS2 | 95.10 ± 0.82 ^a | 10.40 ± 0.46 ^a | 71.75 ± 0.21 ^b |
| CS3 | 95.27 ± 0.49 ^a | 10.50 ± 0.30 ^a | 84.75 ± 1.48 ^b |
| PS1 | 96.93 ± 0.64 ^a | 10.03 ± 0.21 ^a | 60.6 ± 0.42 ^a |
| PS2 | 96.33 ± 0.15 ^a | 10.80 ± 0.20 ^a | 82.45 ± 1.48 ^b |
| PS3 | 94.97 ± 0.75 ^a | 10.80 ± 0.75 ^a | 72.2 ± 2.12 ^b |

Results are presented as mean ± standard deviation of three replicates. Values with same letters are not significantly different at 5% level.

moisture content of the pulp varied from 94.97 ± 0.75% (w.b.) to 96.93 ± 0.64% (w.b.), the final moisture content of the developed packaging material was in the range of 9.50 ± 0.30% (w.b.) to 10.80 ± 0.75% (w.b.) and showed no significant difference between the quantity or type of starch added. Similar results were also reported by Salgado et al. (2008) for composite trays based on cassava starch and cellulose fibers. The study reported a moisture content ranging from 10.35 ± 0.12 (w.b.) to 10.81 ± 0.01 (w.b.) and no significant correlation were found between moisture content and amount of starch added.

Cellulose and starch-based materials are prone to moisture and water damage, which is one of their major limitations. To assess the response of the biodegradable material to water exposure, a water resistance test was conducted using contact angle analysis. As per the available literature, a higher value of contact angle indicates greater hydrophobicity of the material, and vice versa (Pan et al., 2016). The contact angle of the samples varied from 62.95 ± 3.75° for the control to 84.75 ± 1.48° for CS3. When a droplet of water is placed on a surface made of polymer, there is an intermolecular interaction that occurs between the molecules present in the water and the surface of the polymer. The strength of this interaction is dependent on the properties of both the solid surface and the liquid. The major constituent of tender coconut husk are cellulose fibers, which comprise around 44–45% of its composition followed by lignin (37%) (Pandiselvam et al., 2023). Cellulose is the primary

component of natural fibers and is hydrophilic in nature due to the abundance of hydroxyl groups (OH). Whereas, lignin is a highly complex polymer composed of phenylpropane (C9) units that are randomly branched. It is considered the most intricate polymer among all naturally occurring high-molecular-weight materials. Due to its hydrophobic nature, lignin hinders the penetration of water through cell walls.

There was an increasing trend in the hydrophobicity observed on the developed samples with the addition of starch particles. The contact angle of the developed packaging material increased from $68.9 \pm 2.40^\circ$ for CS1 to $71.75 \pm 0.21^\circ$, $84.75 \pm 1.48^\circ$ respectively for CS2 and CS3. A similar increase from $60.6 \pm 0.42^\circ$ for PS1 to $72.2 \pm 2.12^\circ$ for PS3 were also observed. The presence of numerous hydrophilic hydroxyl groups in native starch results in a high level of hydrophilicity. The presence of these hydroxyl groups leads to the formation of robust intermolecular and intramolecular hydrogen bonds within the starch molecules resulting in low solubility in water at normal room temperature (Wang et al., 2020). However, when starch is heated in an aqueous dispersion, it absorbs water and swells, causing the granules to eventually collapse and gelatinize. As the mixture cools, the starch molecules recombine through hydrogen bonds, resulting in the formation of a white precipitate called retrogradation, which increases the hydrophobicity of the starch and reduces its water-binding capacity (Dai et al., 2019). By incorporating starch into the polymer of papers made from cellulosic fibers, the water resistance of the paper was improved. This can be attributed to the significant bonding between the starch and fibers, which hindered the water molecules from interacting with the paper. In essence, the hydrogen bonds between the starch and fibers contributed to the enhanced water resistance of the cellulosic papers (Li et al., 2018; Ghanbarzadeh et al., 2011). In a similar study, Semlali Aouragh Hassani, Salim (Semlali Aouragh Hassani et al., 2022) reported an increased hydrophobicity from $67.87 \pm 1.91^\circ$ when the cellulosic paper were coated with starch particles. Moreover, incorporation of starch into the matrix significantly changed the surface morphology of the paper as evident from the SEM images (Fig. 4). The addition of starch led to a reduction in surface roughness. However, despite this reduction, nano roughness still persisted on the film surfaces leading to the formation of small air-filled pores. It is important to note that air within these pores is highly hydrophobic, resulting in a consistent increase in the contact angle (Song and Rojas, 2013).

3.3. X-ray diffraction spectroscopy (XRD)

X-ray diffraction spectroscopy (XRD) was used to analyze the

crystalline characteristics and confirm the presence of key molecules in the developed composite sheets made using tender coconut husk and intended to develop biodegradable cutlery. Fig. 2 show the X-ray grams of different samples for a better understanding of the changes in the crystalline properties during the addition of starch additives. The XRD data show that all the samples, including the control, had the highest crystalline peak in the range of angle 22° , it originates from (200) crystal plane, indicating the presence of cellulose type I in the developed material (Musikavanhu et al., 2019). Cellulose type I, also known as alpha-cellulose, has a high degree of polymerization and strong nature, making it an ideal material for packaging applications (Muthamma and Sunil, 2022). The diffractogram shows that the amorphous peaks were in the range of angle 16° and became more crystalline with the addition of both starches. The highest intensities were observed in PS3 and CS3, indicating the addition of foreign matter to the base material. The amorphous peak at the range of angle 16° became narrower compared to control, and the prominent crystalline peak at 22° became narrower and sharp, indicating an increase in crystallinity. The crystallinity index (CI) of all the samples was calculated using the method mentioned by Ruland 1961 (Yatsenko and Medvedeva, 2019), as shown in Table 4. The results show that CS3 had the highest CI of 73.35, while the control sample had the lowest CI of 64.43 where as the PS3 sample had a CI value of 66.74, which is in line with a study reported by (Salim et al., 2023). The increase in crystallinity index might be due to the proper doping of corn starch into the cellulose matrix, which decreased the amorphous region and the composite porosity (Vaezi et al., 2019). A similar trend was observed for the potato starch samples, indicating that potato starch and corn starch had a similar effect on the crystalline properties of the developed cellulosic paper. However, when added in the same percentage, corn starch-based samples had a greater effect on CI. It is clear

Table 4
Crystallinity index of developed cellulosic material.

| Sample | Crystallinity index (CI) |
|---------|--------------------------|
| Control | 64.43 ^b |
| CS1 | 68.36 ^a |
| CS2 | 68.53 ^a |
| CS3 | 73.35 ^b |
| PS1 | 65.48 ^a |
| PS2 | 65.42 ^a |
| PS3 | 66.74 ^b |

Values with same letters are not significantly different at 5% level.

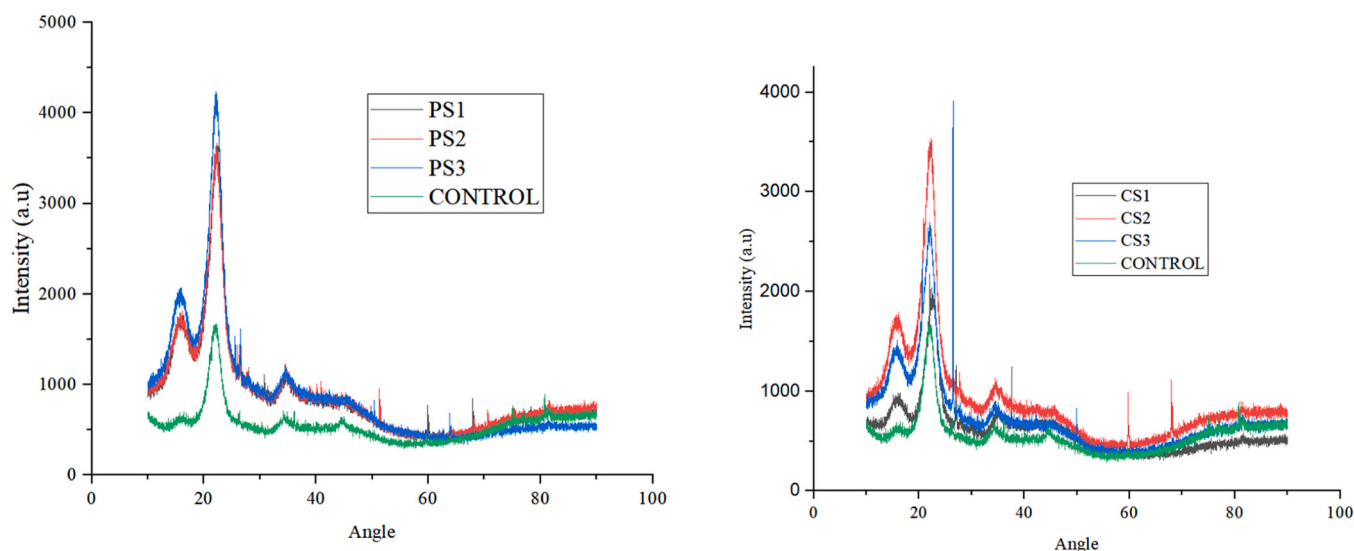


Fig. 2. XRD Patterns of samples coconut husk-based paper with (a) corn starch and (b) potato starch as additives.

that potato starch is not detrimental to the crystalline structure since it does not alter the CI to a larger effect (Yan et al., 2016). The XRD data confirmed the presence of both starches and their molecular-level interaction with the additives. It also indicated that the mixing was proper and facilitated the impregnation of gelatinized starches into the cellulose matrix.

3.4. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectroscopy was used to study the cellulose-starch interaction in the developed paper. Fig. 3 displays the FTIR spectra of coconut husk and the biocomposite fibers produced from tender coconut husk by starch incorporation. The spectra exhibit a distinct band at 3310 cm^{-1} and 3315 cm^{-1} . The broad peak observed at this range is caused by hydrogen-bonded hydroxyl groups. These hydroxyl groups are involved in the intricate vibration stretching patterns of both unbound and bound hydroxyl groups, which collectively form the main structure of starch (Salleh et al., 2009) and cellulose (Hinterstoisser and Salmén, 1999). This suggests that the fibers contain hydrophilic OH groups, which are primarily responsible for the film's ability to absorb moisture and hygroscopic nature. The bending vibration of the hydroxyl bond (O-H) can be observed in the range of $1631\text{--}1648\text{ cm}^{-1}$, and this is associated with the absorption of water molecules in the amorphous regions of starch (Beh et al., 2021). Another common band observed is the vibration peak at 1025 cm^{-1} and 1312 cm^{-1} is characteristic of anhydroglucose O-C stretching (Balakrishnan et al., 2018) and C-O stretching (Senthil Muthu Kumar et al., 2018) in cellulose. The peak at 1427 cm^{-1} in the FTIR spectra is attributed to the asymmetric bending vibration of the CH_2 group (Henryk Kasprzyk, 2004). This peak indicates the presence of the cellulose component in the composite material. The intensity and position of this peak can provide information about the crystallinity and degree of order in the cellulose component (Sunardi et al., 2019). Moreover, it can also indicate the effectiveness of the bonding between the cellulose and starch components in the composite material. The characteristic band of $1414\text{--}1417\text{ cm}^{-1}$ is attributed to the presence of methylene groups of the α -D-glucose monomers of starch, which shows the bending vibration of Methyl- CH_2 (Beh et al., 2021).

3.5. Scanning electron microscopy

The physical structure of paper is essential to understanding their properties and potential applications. One effective method of analyzing the structure of paper is through micrograph analysis. This study utilized

scanning electron microscopy (SEM) to observe the physical characteristics of cellulose-starch based biocomposite paper. Fig. 4 displays the SEM images of the control, corn starch (CS3), and potato starch (PS3) blend samples. The SEM images show that the blend films were homogeneously prepared, meaning the distribution of cellulose fibers and starch granules was consistent throughout the film. Furthermore, the micrographs revealed that the phase structures of the cellulose-starch blend paper varied significantly depending on the type of starch used. Specifically, the micrographs of the blend paper containing corn starch and potato starch displayed distinct phase structures. This suggests that the type of starch used has a significant effect on the physical structure of the developed paper. The findings of this study have important implications for the development of biocomposite films. By understanding the physical properties and structural characteristics of the paper, researchers can optimize their processing and performance in various applications (Mathew et al., 2006). Additionally, micrograph analysis can provide insights into the surface morphology and roughness of the blend paper, which can affect their adhesion and coating properties.

3.6. Soil burial test

The use of biodegradable polymers is increasing because of their environmental advantages. These polymers can decompose naturally and release natural substances such as carbon dioxide, nitrogen, water, biomass, and inorganic salts as byproducts (Hanani et al., 2018). So, natural biodegradability under soil conditions is an essential characteristic that has to be projected. In this study, samples, namely control, PS3, and CS3, were subjected to a soil burial test, and images of residues after 20 days were taken and shown in the Table 5. From the images, it is visible that all samples have almost similar biodegradability. Almost 70% of the material was degraded over the period, which indicates the suitability of the material for biodegradable cutlery preparation. Similar reports on soil burial tests of cellulose suggest that the material can be 50% degraded within the first 20 days, which almost agrees with the obtained results (Erdal and Hakkarainen, 2022).

4. Conclusion

In conclusion, the mechanical properties of cellulose-starch based composite packaging paper play a crucial role in ensuring their effectiveness as production of biodegradable cutlery. Tensile strength and elongation at break are crucial properties that determine the paper's ability to withstand stress and deformation during transportation and

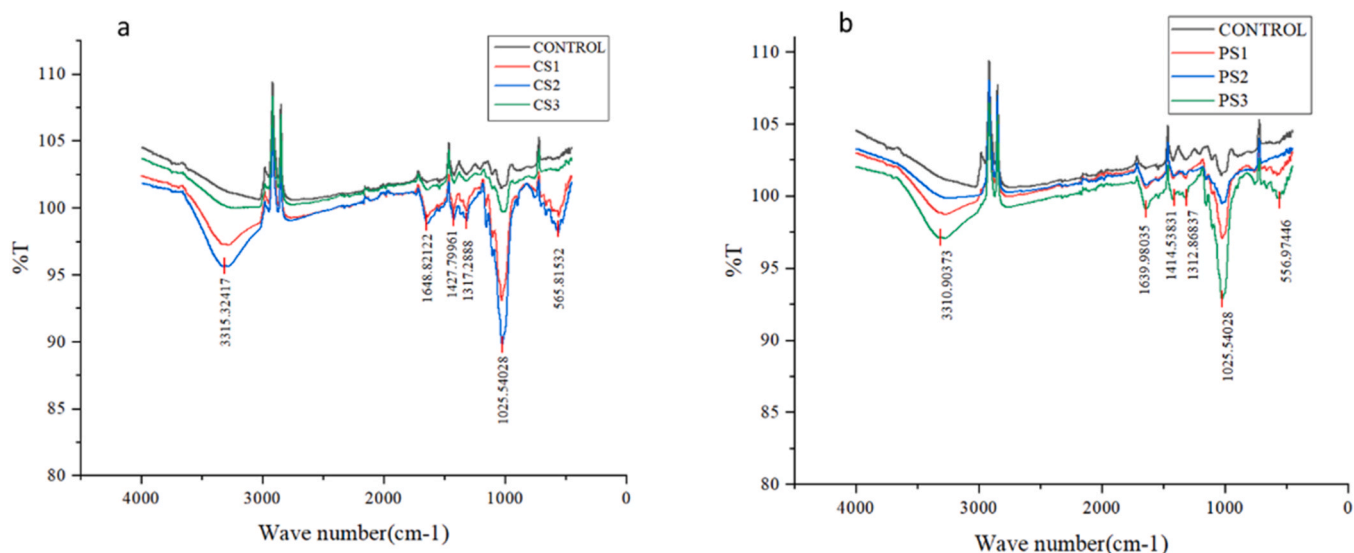


Fig. 3. FT-IR spectra of coconut husk-based paper with corn starch (a) and potato starch as additives.

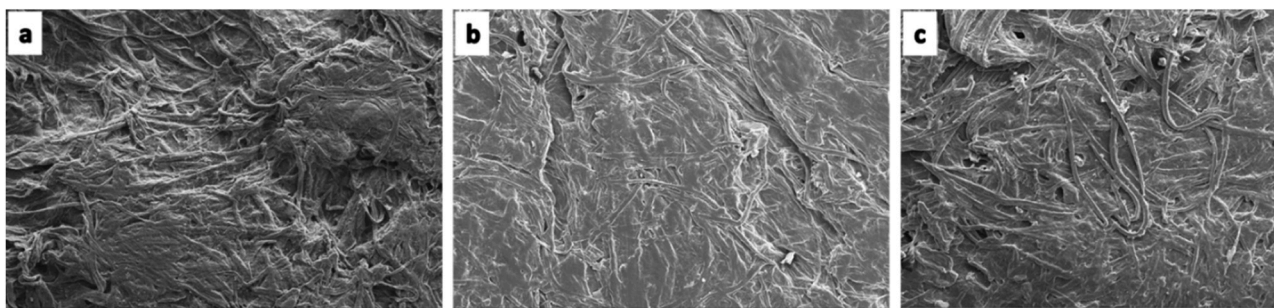
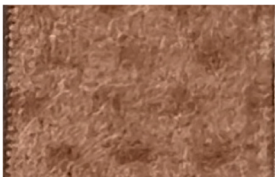

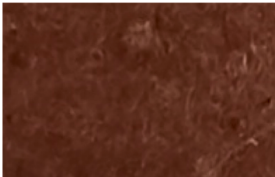





Fig. 4. : SEM images of the developed packaging material, (a)control, (b) corn starch as additive (15% incorporation), and (c) potato starch as additive (15% incorporation).

Table 5
Soil burial tests for developed composite material.

| Sample | Day 1 | Day 20 |
|---------|---|---|
| Control |  |  |
| PS3 |  |  |
| CS3 |  |  |

storage. Tensile strength and elongation at break vary with starch concentration, highlighting the need for precise control to achieve desired mechanical characteristics. Moisture content remains consistent. The tensile strength and the elongation percentage of the developed biocomposite paper varied from 12.45 ± 1.69 MPa to 9.52 ± 4.30 MPa and $9.76 \pm 0.99\%$ to $15.52 \pm 3.27\%$ respectively. Furthermore, water resistance is an important characteristic to consider when developing cellulose-starch based biodegradable paper, as they are vulnerable to moisture and water. The developed paper had a hydrophobicity value falling below 90° which was one of the major drawbacks of the developed paper. The hydrophobicity of the material can be improved by effectively coating the paper with a suitable hydrophobic polymer, and further studies are needed to investigate the effect of coating as it can help in developing a packaging material with better mechanical and physical properties. Soil burial tests affirm the biodegradability of the materials. The results suggest that the amount of starch added to the paper matrix should be carefully controlled to achieve the desired mechanical properties. Overall, the findings of this study contribute to the understanding of the mechanical and moisture properties of cellulose-

starch based composite paper and can aid in the design of biodegradable packaging materials and/or cutlery for specific applications.

Ethics approval and consent to participate

Not applicable.

Consent for publication

All authors agreed on the publication of this research work.

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CRedit authorship contribution statement

R. Pandiselvam- Conceptualization, Methodology, Investigation, Resources, Writing original draft; M.P. Harikrishnan - Methodology, Investigation, Writing original draft; Anandu Chandra Khanashyam -Methodology, Data Analysis, Review & Editing; M. Basil - Methodology, Investigation; M. Anirudh - Methodology, Investigation; Resources; M.R. Manikantan: Methodology, Investigation, Supervision; Anjineyulu Kothakota: Data analysis, Resources, Validation, Investigation.

Declaration of Competing interest

The authors declare that they have no conflict of interest.

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Competing interests

The authors declare no competing interests.

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