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The Effect of Hygroscopic Properties on the Hygromorph of Pla/Nanolignin Smart Biocomposite

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Abstract—The field of Hygromorph BioComposites (HBC) is gaining traction due to their unique biological functionality resulting from the hygroscopic anisotropic properties of natural fiber ultrastructures. These properties, characterized by moisture-induced changes in stiffness, make them responsive to humidity variations. Although the use of HBC is a new development, there is still a lack of research on how they respond to changes in humidity levels. This study aims to fill this gap by investigating how the addition of nanolignin and epoxidized palm oil (EPO) as a plasticizer affects the hygroscopic properties of 3D-printed PLA/nanolignin biocomposites. The research also seeks to identify the optimal 3D printing layer height parameter that significantly impacts the hygroscopic characteristics of PLANanolignin biocomposites. Additionally, the study aims to determine the maximum water absorption capacity of the resulting PLA/Nanolignin smart biocomposites. These objectives were accomplished through the fabrication of PLA/Nanolignin filament using an extrusion process, followed by the production of 3D-printed biocomposites utilizing fused deposition modeling (FDM) techniques. Among the tested formulations, PLA supplemented with nanolignin (PLANL) exhibited the highest water absorption capacity at 7.39%, with a printing layer height of 0.6 mm. Scanning electron microscopy (SEM) was used to study the morphological features of the biocomposites. The results of this study provide new insights into the relationship between hygroscopic behavior and material composition, and they also offer guidance for the design and development of 3D-printed PLA/nanolignin biocomposites with improved hygroscopic properties.

Keywords—Hygromorph BioComposites (HBC), hygroscopic properties, printing layer height, water absorption capacity

Introduction

Starting from 2013, 4D printing has emerged as an innovative trend that distinguishes itself from traditional 3D printing. In contrast to 3D printing, where objects are produced in a fixed form, 4D printing introduces a transformative element. It allows structures to adapt their shape, structure, or function in response to external stimuli after they have been printed, introducing time as the fourth dimension in this context. Essentially, it operates as a programmable 3D printing process, where the printed material interacts with environmental factors like pH, temperature, mechanical forces, humidity, and more. Consequently, it can deform or change its shape accordingly after the initial fabrication. It's important to note that natural fibers, including hemp, flax and wood have traditionally been susceptible to moisture-related issues when used in composite materials, which can compromise the mechanical properties and overall durability of biocomposite materials. However, recent developments have given rise to self-shaping wood and moisture-responsive natural fiber biocomposites which often referred to as hygromorph biocomposites [1].

Electro-Active Polymer (EAP), hydrogel, Shape Memory Polymer (SMP)and the relatively recent innovation of Hygromorph BioComposites (HBC) have found applications in this regard [1], [2]. Among these materials, HBC stands out as an environmentally friendly, intelligent, and sustainable option that harnesses locally available renewable energy sources. These self-contained detectors and actuators possess the unique ability to operate without the need for additional power to control electronic or mechanical functions. Thanks to the hygroscopic properties inherent in their natural fiber composition and intricate architecture, they exhibit biological functionality. Consequently, they can be employed in self-deployable structures, adaptable medical devices, soft robotics, as well as sensors and actuators. Notably, HBC boasts significantly higher actuation capability compared to conventional matrix-based shape-changing metamaterials due to its superior strength and stiffness [3]. HBC qualifies as a moisture-responsive material, readily undergoing swelling, shape modification, and functionality alteration when exposed to liquid or humidity-based stimuli [3]. Materials responsive to water or moisture hold considerable appeal due to their widespread applicability to a wide range of stimuli-driven scenarios. Hydrogels, for instance,are known for their exceptional moisture responsiveness [4]. Furthermore, research by Le Duigou et al. (2021) has pointed out that HBC, with its bilayer microstructure inspired by biological hydraulic actuators like pinecones, can be activated by changes in humidity or a combination of moisture and temperature cues. The heightened responsiveness to relative humidity in HBC leads to faster moisture transport and material expansion, enhancing their performance [4].

PLA, a polymer that is bio-based can serve as a shape-memory material in 4D printing [5]. However, PLA faces significant drawbacks such as high costs, brittleness, slow crystallization, and limited heat resistance, which have hindered its widespread commercial adoption [14]. Leja et al. (2010) have highlighted PLA's tremendous potential due to its outstanding qualities, encompassing excellent mechanical properties (especially modulus and strength), ease of processing, impressive transparency and degradability [6], [7]. Concerning applications, PLA exhibits the highest flexural and tensile strengths among biodegradable thermoplastics used in 3D printing [8].

Lignin, derived from agricultural and industrial waste remnants, is recognized as a biopolymer [5]. Recent scientific investigations have been focused on creating composites using bio-based additives such as cellulose, lignin and their nanoscale counterparts to address these limitations and produce PLA-based materials with improved mechanical and physicochemical characteristics. Nanolignin, as opposed to larger-scale raw lignin, possesses smaller and more uniform particle sizes, which result in greater compatibility with PLA [9]. The incorporation of lignin into bio-based polymers holds the potential to yield renewable composites with enhanced properties [10]. Epoxidized palm oil, a derivative of glycerol esters containing both unsaturated and saturated fatty acids, is favored by many chemical industries due to its eco-friendly, biodegradable, renewable, and readily available source material [11]. Plasticizers like epoxidized palm oil (EPO) have been employed to enhance the characteristics of polymer blends [12].

Depite the current global environmental challenges, there is a notable absence of a sustainable alternative rooted in biobased materials. Additionally, there has been limited research conducted on 4D printing of moisture-responsive actuators using natural fibers like lignin. Lignin, an abundant natural resource, holds promise for reducing reliance on non-renewable materials when incorporated into biocomposites. Lignin possesses inherent hygroscopic properties, allowing it to absorb and release moisture from the environment. This characteristic plays a pivotal role in the development of hygromorph materials, which exhibit reversible shape changes or actuation in response to humidity fluctuations.

While natural fibers introduce a novel reinforcement material for polymeric composites, they come with their challenges, including poor interfacial bonding and the hydrophilic nature of these fibers. These properties can lead to inadequate bonding with the polymeric matrix, and water absorption has long been recognized as a limitation in natural fiber-reinforced composites. Consequently, this study investigates the water absorption capacity of 3D printed PLA/Nanolignin biocomposites.

Furthermore, this research is motivated by the nascent stage of studies on hygroscopic behavior of these materials and the relative lack of research into PLA/Nanolignin biocomposites. Examining water absorption in PLA/Nanolignin biocomposites is of paramount importance as it provides insights into the long-term durability and performance of these materials in wet or humid environments. Water absorption can profoundly impact mechanical, thermal, and barrier properties and may lead to swelling and dimensional changes. This study specifically focuses on creating PLA/Nanolignin/EPO biocomposites as 3D printing filament via the Fused Deposition Modeling (FDM) process, with the goal of identifying the optimal 3D printing layer height parameter, a significant factor influencing the hygroscopic characteristics of PLA/Nanolignin biocomposites. Additionally, the study seeks to determine the maximum water absorption capacity of the resulting smart biocomposites.

Methodology

In this investigation, we utilized commercial-grade PLA in pellet form (Ingeo PLA 2003D, NatureWorks Co. Ltd, Nebraska, USA). Nanolignin, in powder form, was provided by Sigma-Aldrich. Epoxidized palm oil (EPO) with a density of 0.886 g/mL and an oxirane oxygen content of 2.84 was sourced from Budi Oil Enterprise Sdn Bhd, Telok Gong, Port Klang, Selangor, Malaysia.To prepare the samples, the PLA pellets were first subjected to oven drying at 60 °C for 3 hours to eliminate any moisture content. Subsequently, they were mixed with nanolignin powder at varying weight fractions (ranging from 1 to 5 phr). The composition details of the PLA/Nanolignin/EPO biocomposite filament can be found in Table 1 [13].

Table 1 Composition of PLA/Nanolignin/EPO biocomposite filament.

Biocomposite Designation	PLA (phr)	Nanolignin (phr)	EPO (phr)
PLA	100	-	-
PLAE	100	-	5
PLANLE	100	1	5
PLANL	100	1	-

The mixtures were subsequently extruded via a FILABOT EX6 Extruder at varying temperatures: 180 °C (front), 190 °C (middle), 180 °C (back), and 50 °C (feed). The rotational speed of the extruder motor ranged from 40 to 50 rpm. The resulting extruded filaments were spooled and guided through an airpath for cooling. After each run, the extruder was purged with PLA to eliminate any residual material from the previous process. Biocomposite filaments that met these criteria were utilized via a fused deposition modeling (FDM) 3D printer, specifically the Ender 3 Pro.Furthermore, concerning the water absorption assessment, 3D printed samples were manufactured using five distinct layer heights, each having precise dimensions of 70 mm by 25 mm by 1 mm, along with printing parameters detailed in Table 2.

Table 2 Parameter of FDM process via Ender 3 Pro.

Printing Parameters	Value
Nozzle temperature (°C)	200
Infill density (%)	20
Infill pattern	Triangles

Layer height (mm)	0.2, 0.3, 0.4, 0.5, 0.6
Raster orientation	45°
Printing orientation	Flat
Printing direction	0°/90°
Print speed (mm/s)	70
Plate temperature (°C)	60
Shell wall thickness	0.8

To analyze the samples, two evaluations were conducted to assess the hygroscopic properties of PLA/Nanolignin/EPO biocomposites and the impact of nanolignin as a filler in the PLA matrix, along with EPO as a plasticizer in humid conditions. The first evaluation measured the water absorption capacity, following the ASTM D570 standard. The five specimens were immersed, each with varying printing layer heights (0.2 mm, 0.3 mm, 0.4 mm, 0.5 mm, and 0.6 mm), in distilled water at room temperature for 28 days. These specimens had dimensions ofL: 70 mm, t: 1 mmand W: 25 mm [2]. Periodically, removed and dried the specimens before weighing and characterization. The percentage gain in weight at any time "t" was calculated using Eq (1) as "Mt."

$$M_t\,(\%) = \frac{W_t - W_0}{W_0} x\ 100 \qquad (1)$$

The maximum water absorption was calculated using the average weight of the specimen after water absorption (W_t) and the initial weight of the dry material before immersion (W_0). This calculation was based on five consecutive measurements taken over a period of 28 days [15]. To examine the morphologies of the PLA/Nanolignin biocomposites, Scanning Electron Microscope (SEM) JSM 5600 was utilized. The samples were cut into smaller pieces at the fracture cross-section area and then mounted on specimen stubs. To ensure the samples had conducting properties, their surfaces were coated with palladium using a sputter coating process. These images were captured at an accelerating voltage of 7.0kV and observed at various magnifications.

I. Results And Discussion

The influence of nanolignin and EPO on the hygroscopic properties of 3D printed PLA/Nanolignin biocomposites was investigated by assessing water absorption compared to pure PLA biocomposites.

As shown in Figure 1, a clear illustration revealed the optimal 3D printing layer height for PLA/Nanolignin biocomposites to be 0.6 mm. Notably, a noteworthy trend emerged, particularly in the cases of PLA, PLAE, PLANLE, and PLANL samples. The pattern indicated that an increase in 3D printing layer height corresponded to an augmentation in the water absorption capacity of the printed specimens.

This phenomenon could be ascribed to structural modifications resulting from varying the layer height. Elevated layer height led to thicker individual layers in the printed specimen, consequently creating a higher prevalence of interlayer gaps or voids within the structure. These voids and gaps served as pathways facilitating easier water infiltration into the specimen. The increased space between the layers allowed water to traverse the material more readily, thereby enhancing its water absorption characteristics. Furthermore, the change in layer height directly influenced the overall density and porosity of the printed specimen. Thicker layers during printing likely resulted in a less densely packed structure with increased porosity. This heightened porosity provided additional room within the material for water absorption and retention.

To summarize, Figure 1 highlighted the pivotal role of 3D printing layer height in determining the water absorption properties of PLA/Nanolignin biocomposites. This observation contributes to our understanding of how printing parameters affect material characteristics in additive manufacturing, potentially allowing for tailored material properties for specific applications

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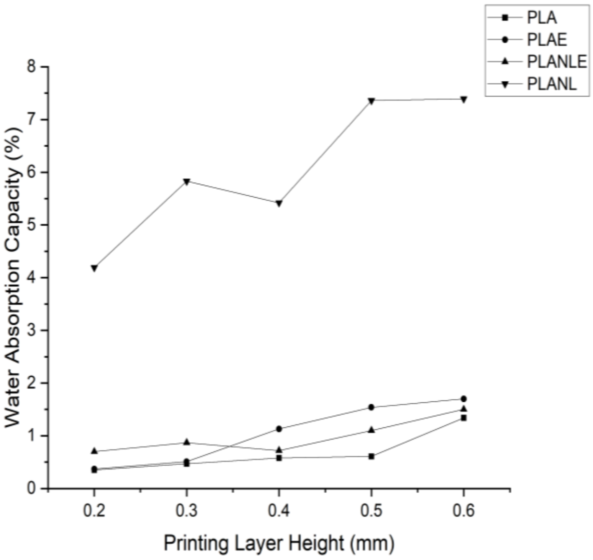

Fig. 1.The analysis of printing layer thickness and water absorption3D printed PLA/Nanolignin biocompositesspecimens.

Table 3 in the research unveiled intriguing findings concerning the water-absorption characteristics of a material referred to as PLANL when compared to other materials like PLA, PLAE, and PLANLE, across various printing layer heights. Remarkably, PLANL consistently demonstrated significantly higher water absorption capabilities, exhibiting an impressive increase of up to 7.39% in comparison to the other materials. This distinction emphasized the substantial impact of nanolignin on the water absorption behavior of composite materials.

Nanolignin, characterized by its extensive surface area, exhibited a remarkable capacity to absorb and retain water molecules. When incorporated into a composite structure alongside PLA, it played a pivotal role. This combination resulted in the formation of a complex network of tiny channels or voids within the composite's structure. An especially noteworthy attribute of nanolignin was its inherent hydrophilicity, indicating its natural attraction to water, effectively drawing water molecules towards it. As a result, the composite material benefited from enhanced water absorption due to this hydrophilic property. The heightened water absorption observed in PLANL stemmed from the synergistic interplay between the nanoscale voids generated by nanolignin and its hydrophilic nature. These combined effects collectively amplified the water absorption potential of the composite material. In contrast, the lower water absorption capacities exhibited by PLA, PLAE, and PLANLE could be attributed to the hydrophobic characteristics of PLA and EPO. As inherently hydrophobic materials, they displayed limited affinity for water molecules, thus exhibiting resistance to water absorption. This dynamic changed with the introduction of EPO and the combination of EPO and nanolignin into the PLA matrix. This modification altered the surface properties of the composite, resulting in an overall reduction in its water absorption capacity. In conclusion, the optimal printing layer height for 3D printed PLA/Nanolignin biocomposites was determined to be 0.6 mm.Notably, PLANL outperformed the other materials, achieving a maximum increase of 7.39% in water absorption capacity. This study illuminated the intricate relationship between material composition, hydrophilic characteristics, nanoscale structures, and water absorption behavior in composite materials, paving the way for the development of advanced functional materials with tailored water interaction properties.

Table 3

The water absorption capacity of 3D printed PLA/Nanolignin biocomposites specimens.

Printing Layer Thickness (mm)	Water Absorption Capacity (%)			
	PLA	**PLAE**	**PLANLE**	**PLANL**
0.2	0.35	0.37	0.7	4.19
0.3	0.47	0.51	0.87	5.83
0.4	0.58	1.13	0.72	5.42
0.5	0.61	1.54	1.1	7.36
0.6	1.34	1.70	1.5	7.39

The cross-sectional morphologies of fractured specimens from 3D printed PLA/Nanolignin biocomposites are depicted in Figure 3. Scanning electron microscope (SEM) images were taken at 100x and 250x magnifications within the internal fragments of the fractures.

Examining Figure 3 (a), the pure PLA's fractured surface displayed a remarkably uniform texture, indicating a brittle break with its smooth appearance. However, elongated polymer fibrils were also noticeable on this surface. Moving to Figure 3 (b), the SEM images for PLAE exhibited a fracture pattern similar to pure PLA, with thin, elongated fibrils present. Notably, distinct regions or agglomerates suggested the presence of EPO polymer fibrils dispersed within the PLA matrix as filler material.

Figure 3 (c) presented a distinct fracture morphology for PLANL, contrasting with pure PLA and PLAE. The incorporation of nanolignin particles resulted in a more brittle and intricate microstructure, evident from the rougher texture on the fracture surface, along with dispersed nanolignin particles. Lastly, in Figure 3 (d), PLANLE displayed a combination of features observed in PLAE and PLANL. The fractured surface indicated the presence of both EPO and nanolignin particles, along with potential interaction zones between the fillers and the PLA matrix.

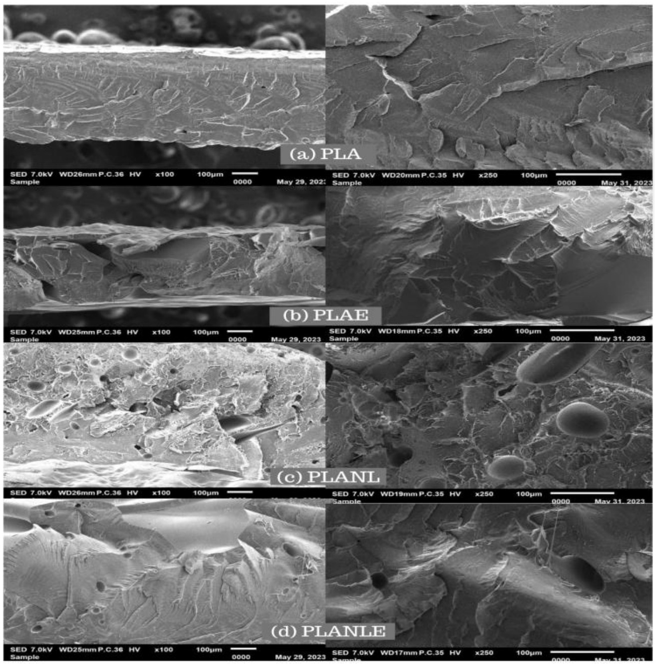

Fig. 3.3D printed PLA/Nanolignin biocomposites of specimens' fracture at magnification of 100x and 250x for PLA (a), PLAE (b), PLANL (c) and PLANLE (d).

Conclusion

Overall, the study's outcomes advocate for the utilization of PLA filaments integrated with nanolignin as a strategy to achieve enhanced hygroscopic properties. This advancement holds significant promise across a diverse range of applications, including biomedical devices, packaging solutions, food preservation methods, and automotive interior components. The enhanced hygroscopic capabilities provided by the PLA/Nanolignin biocomposites represent a noteworthy technological breakthrough that can lead to the development of more efficient and reliable products in various industries.

In the broader context of 4D printing, the investigation into the hygroscopic properties of these advanced materials adds a new dimension to the potential applications of this technology. The dynamic adaptation of material properties in response to environmental changes, enabled by the combination of 4D printing and hygromorph biocomposites, offers exciting prospects for creating self-regulating and responsive structures that can revolutionize multiple sectors.In summary, the research sheds light on the intricate relationships between 4D printing parameters, material composition, and hygroscopic characteristics. By pinpointing the optimal layer height and showcasing the advantageous properties of nanolignin-infused PLA, this study contributes to the advancement of materials science, offering a pathway to more sophisticated and versatile applications in the fields of engineering, medicine, packaging, and beyond.

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