Effect of Unbleached and Bleached Softwood Cellulose Pulp Fibers on Poly(lactic acid) Properties

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Global regulations are guiding society towards more sustainable material solutions. This increasing awareness of the need for environmentally friendly alternatives has led to a greater emphasis on biocomposites, which combine natural fibers with bio-based polymers. This study investigates how bleached softwood pulp fibers (BSWPF) and unbleached softwood pulp fibers (UBSWPF) affect the characteristics of poly(lactic acid) (PLA)-based biocomposites. UBSWPF is a more cost-effective option because it is manufactured with less processing steps than BSWPF. However, it is largely unexplored as a reinforcement in biopolymers. Through investigating the mechanical, thermal, and morphological aspects of the biocomposites, this study showed that UBSWP increased the modulus and impact strength of the PLA biocomposites better than BSWPF. The impact strength, modulus, and tensile strength of PLA-BSWPF and PLA-UBSWPF improved as the fiber content increased. However, a decrease in tensile strength was seen at higher percentages of UBSWPF in PLA. Despite the decrease in tensile strength at higher UBSWPF concentrations, both types of fibers improved the mechanical properties of the biocomposites, demonstrating a potential sustainable reinforcing material for PLA biocomposites.

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INTRODUCTION

There has been a focused effort in replacing polymers with bio-based and biodegradable materials. Poly(lactic acid) (PLA) has emerged as a promising contender to replace fossil-based polymers in various applications (Naser *et al.* 2021; Freeland *et al.* 2022; Swetha *et al.* 2023). As an eco-friendly polymer, the production and use of PLA contributes to significant energy savings and a decrease in greenhouse gas emissions (Balla *et al.* 2021). When compared to various traditional plastics derived from petroleum, PLA manufacture consumes 25 to 55% less fossil fuel energy. Furthermore, utilizing renewable energy sources, like wind power, during various production stages can lead to an approximately 90% reduction in fossil energy consumption (Rajeshkumar *et al.* 2021).

However, PLA's susceptibility to brittleness hinders its widespread adoption (Yu *et al.* 2023). To address this limitation, substantial research has been conducted to improve the mechanical properties of PLA through the incorporation of natural fibers as reinforcement (Aliotta *et al.* 2019; Oksman *et al.* 2003). Studies have demonstrated that the mechanical properties of PLA are enhanced through the incorporation of natural fibers

as reinforcement (Ilyas *et al.* 2021; Tümer and Erbil 2021).

Among natural fibers, plant and wood-based fibers have been thoroughly investigated as reinforcement for biocomposites. Although plant-based fibers have shown promising results (Joseph *et al.* 1999; Baghaei *et al.* 2013; Orue *et al.* 2018; Yusoff *et al.* 2023), their practical applicability is limited due to various issues, such as low cost-effectiveness and competition with food crops (Madsen and Gamstedt 2013). Here, the competition with food crops refers to using the same land, water, and nutrients for growing both food and non-food crops. Notably Canada, Finland, Russia, Sweden, and the United States of America are some of the countries where wood-based fibers offer an economically feasible solution because of their widespread availability. There are two main types of wood fibers: softwood and hardwood fibers. There has been some research with hardwood fibers as a reinforcing material in biocomposites (Marc Delgado-Aguilar *et al.* 2018; Peltola *et al.* 2019). Although BSWPF and UBSWPF are important raw materials for paper production, their use in biocomposites reflects the evolving market dynamics and technological advancements. With the digitalization trend and the declining use of traditional paper products (Hassan *et al*. 2021), innovative applications for pulp fibers are increasingly important. Several companies, such as UPM, are exploring these new opportunities to create sustainable materials that can meet modern demands.

Softwood fibers have seen more interest in research (Garcia *et al.* 2016; Granda *et al.* 2016; Delgado-Aguilar *et al.* 2017; Tarrés *et al.* 2019; She and Xu 2023) because of their higher availability, which makes them cost-effective. Bleached softwood pulp fibers have shown promising results in improving the mechanical properties of polypropylene (Kalia *et al.* 2011) and PLA (Immonen *et al.* 2019) biocomposites.

Bleaching of wood fibers is done to remove residual lignin and hemicellulose from the structure of the wood fiber (Bernal-Lugo *et al*. 2019; Benali *et al*. 2024). When producing bleached kraft pulp, the Kappa number is typically reduced to a lower level before the bleaching process begins. A lower Kappa number means lower lignin content. Bleaching also reduces the content of hemicelluloses such as xylan and glucomannan, which may affect surface hydrophilicity and surface charges (Esteves *et al*. 2022). The noticeable variation in colour, with UBSWPF appearing darker brown, is mostly due to their higher lignin content. In contrast, bleached fibers have little to no lignin content, resulting in a lighter hue (Oliaei *et al.* 2020). BSWPF and UBSWPF suitability for applications is determined by criteria such as colour needs and strength attributes. When white colour is desired, particularly for applications with aesthetic considerations, bleached fibers are typically used. In contrast, UBSWPF is used in applications requiring more robustness, such as brown packaging materials. Furthermore, UBSWPF has a lower carbon footprint than BSWPF due to the energy-intensive bleaching process that uses chemicals and generates waste (Jour *et al.* 2015; Kuparinen 2019; Karjalainen 2023). A carbon footprint is a measurement of greenhouse gas emissions, among several factors energy use and waste generation influenced the carbon footprint of a product or process.

This work related to the use of UBSWPF as reinforcement in PLA gives a new approach compared to existing research. This study aims to address this gap and delve into the comparative study of the influence of bleached and unbleached softwood pulp fibers on the properties of PLA biocomposites. Through investigating their impact on mechanical, thermal, and morphological aspects, the authors seek to contribute to the development of sustainable and effective strategies for reinforcing biopolymers. The research aligns with the broader objective of advancing the field of biocomposites, with a focus on harnessing the untapped potential of UBSWPF.

EXPERIMENTAL

Materials

PLA Ingeo 3251D from NatureWorks LLC (Blair, NE, USA) with a melt temperature of 169.8 °C was used as a polymer matrix. Kraft pulp fibers were provided by Metsä Fiber; the never dried bleached softwood pulp fibers (BSWPF) in dry material content 30% were from Rauma pulp mill, Finland. The used BSWPF is obtained using the Elemental Chlorine-Free (ECF) bleaching method, which uses chlorine dioxide to minimize harmful chlorinated compounds (Yin *et al*. 2022). Metsä Fiber's Kemi pulp mill (Finland) also provided never dried unbleached softwood pulp fiber (UBSWPF) in dry material content 30%. UBSWPF is obtained through the kraft pulping process, which converts wood chips into pulp using an alkaline cooking liquor (Mboowa 2024). According to the manufacturer, the BSWPF contains no lignin, 15% hemicellulose, and 85% cellulose, and UBSWPF contains 7% lignin, 16% hemicellulose, and 77% cellulose. Before compounding, the fibers were pelletized using a special cone-shaped pelletized modified from KAHL-pelletizer. The pelletizer is explained in more detail in a patent (Sivonen and Valta 2010) and it has been made at VTT. The purpose of pelletizing fibers is to densify the cellulose fibers. The as-received fibers are fluffy, which makes it difficult to feed them during compounding.

Biocomposite Processing

The UBSWPF and BSWPF pellets and the PLA were first dried in a vacuum oven for 50 °C overnight (about 14 h). The fiber pellets were dried because they contained nearly 70% moisture. A large moisture content in fiber could affect the processability of the biocomposites and it has the potential to induce hydrolytic degradation in PLA.

Each recipe presented in Table 1 was compounded using a co-rotation twin-screw extruder (Berstorff ZE 25x33D; Berstorff GmbH, Hannover, Germany) with eight temperature zones. The materials were fed using a gravimetric feeder and the temperature profile was kept between 165 and 190 °C. The screw speed was around 150 to 175 revolutions per minute (rpm).

Table 1. Compositions and Parameters of Compounding of PLA-BSWPF and PLA-UBSWPF Biocomposites

Composition	Sample Name	Flow Rate (kg/h)	Screw Speed (rpm)	Zone Temperatures (°C)
PLA 90 wt% + UBSWPF 10 wt%	PLA 10UB	2.8	150-175	165-175-185-190-190-190-190-185
PLA 80 wt% + UBSWPF 20 wt%	PLA 20UB	3.0		
PLA 75 wt% + UBSWPF 25 wt%	PLA 25UB	3.0		
PLA 90 wt% + BSWPF 10 wt%	PLA 10B	2.8		
PLA 80 wt% + BSWPF 20 wt%	PLA 20B	2.8		
PLA 75 wt% + BSWPF 25 wt%	PLA 25B	2.2		

The PLA-BSWPF and PLA-UBSWPF biocomposites were then put into a vacuum oven again at 50 °C overnight (about 14 h). The dried biocomposites were then injection

molded using Battenfeld injection molding machine (SmartPower 25 – 400 t, Wittmann Battenfeld GmbH, Kottingbrunn, Austria) with temperature profile 195-190-190-190 °C at its four temperature zones. The mold temperature was 35 °C.

The flow rate for PLA-BSWPF was a bit smaller than PLA-UBSWPF due to slightly plasticizing effect of lignin in the PLA-UBSWPF, which is in line with the review article by Fazeli *et al*. (2024).

Characterization

Melt flow index

The melt flow index (MFI) of the biocomposites was determined in accordance with ISO 1133-1 (2011) at 190 °C and 2.16 kg using RAY-RAN Melt Flow Indexer, Model 3A (Industrial Physics, Theme, UK). The MFI is a measurement of the mass of molten material that flows through the capillary tube of a standard die in a 10-min time.

Microtomography

The cross-sectional structure of the samples to visualize the fiber distribution and orientation was studied using a microtomography scanner (µCT) DeskTom 130, RX Solutions, Chavanod, France). A 40 kV acceleration voltage and 4 W electron beam power were used. For each sample 1440 projection images were collected over 360° with a voxel size of 8.0 µm. The exposure time was 1 s and one projection image was averaged from each angular step, resulting in a total imaging time of 24 min for each sample. The sample was placed in the equipment without extra preparation. The entire middle part of the injection-molded dog bone was used, making imaging easy and efficient.

Scanning electron microscopy

The morphology of the injection molded biocomposite samples was examined using a scanning electron microscope (SEM). The analysis focused on the cross-section of samples fractured after dipping them in liquid nitrogen. A JEOL JSM T100 SEM (JEOL Ltd., Tokyo, Japan) was used for this purpose. A thin gold layer with a thickness of 5 nm was placed to the sample surface to prevent surface charging.

Charpy impact strength

Testing for Charpy impact strength was done in accordance with ISO-179. Before testing, the samples were conditioned for five days at 23 °C and a relative humidity of 50%. Using a Charpy Ceast Resil 5.5 Impact Strength Machine (CEAST S.p.a., Torino, Italy), impact strengths were assessed for 10 parallel unnotched specimens in a three-point bend configuration.

Tensile strength and modulus

The injection molded samples were subjected to a five-day conditioning period at 23 °C and 50% relative humidity prior to testing. Tensile testing was performed using an Instron 4505 Universal Tensile Tester (Instron, Norwood, MA, USA). The crosshead rate was set to 5 mm/min, and a 10 kN load cell was used. The strain was measured using an Instron 2665 Series High Resolution Digital Automated Extensometer in compliance with ISO 527 (2012) standard. Each biocomposite was tested with six parallel samples, and the tensile strength and Young's modulus averages and standard deviations were calculated. According to ISO 527 (2012), the recommended dimensions for tensile samples are 4 ± 0.2 mm in thickness, 10 ± 0.2 mm in width and 170 mm in length. These dimensional

tolerances enable consistency and accuracy in mechanical property measurement throughout testing.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to analyse the neat PLA and biocomposite samples using a NETZSCH DSC 204F1 Phoenix 240-12-0287-L equipment (NETZSCH GmbH, Selb, Germany). During the analysis, the samples with ≤ 6 mg weights were exposed to a specified thermal profile. A ramp rate of 10 °C/min was used, starting from 0 °C and to 200 °C. The samples were cooled at a rate of 10 °C/min to 0 °C. Degree of crystallization was calculated using Eq. 1,

$$\text{Degree of Crystallization (\%)} = (\Delta H_m - \Delta H_c) / \Delta H_f * 100 \quad (1)$$

where ΔH_c is the cold crystallization enthalpy, ΔH_m is the melting enthalpy, and ΔH_f is the melting enthalpy of neat PLA (93.6 J/g) (Mohapatra *et al.* 2014).

RESULTS AND DISCUSSION

Figure 1 represents the injection molded samples of PLA-UBSWPF, PLA, and PLA-BSWPF. The dark brown colour observed in the PLA-UBSWPF can be attributed in part to the presence of lignin within the unbleached softwood pulp fibers. However, it is important to recognize that during processing, the lignin undergoes thermal degradation and chemical reactions, leading to the formation of darker compounds. The PLA is transparent and PLA-BSWPF samples have light brown colour.

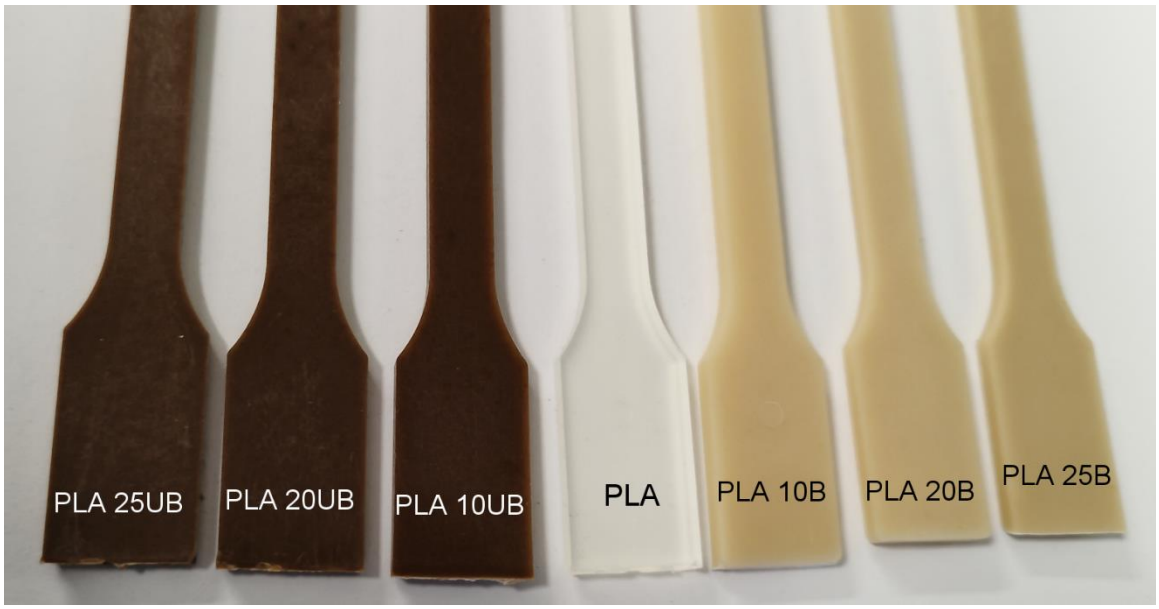

Fig. 1. Visual outlook of injection molded samples

Melt Flow Index

Figure 2 shows that PLA-BSWPF experienced considerable decreases in MFI with increasing fiber content. The MFI of values of PLA 10B decreased 82.7%, PLA 20B by 96.9%, and PLA 25B decreased up to 98.5% compared to neat PLA. PLA-UBSWPF

exhibited a similar but slightly less pronounced trend. PLA 10UB decreased 81.2%, PLA 20UB 94.9%, and PLA 25UB MFI decreased up to 96.8% compared to neat PLA.

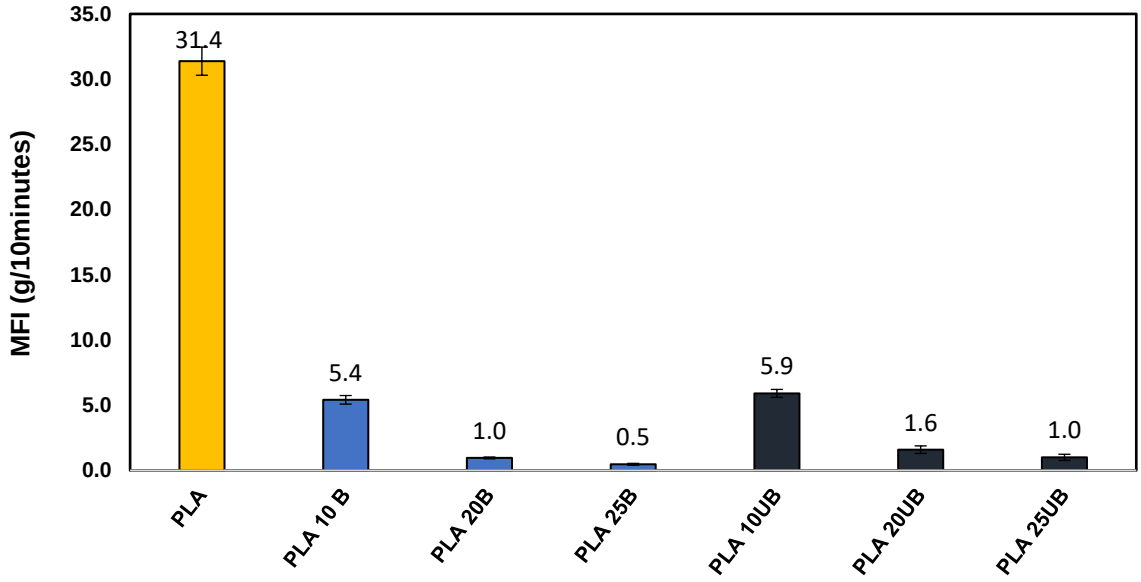

Fig. 2. The melt flow index (MFI) of neat PLA, PLA-BSWPF, and PLA-UBSWPF biocomposites

PLA-UBSWPF has slightly higher MFI than PLA-BSWPF. This is due to the plasticization effect of lignin (Park *et al.* 2018; Domínguez-Robles *et al.* 2020). The addition of BSWPF and UBSWPF in PLA increases viscosity by creating hinderance in material flow in molten state. Furthermore, the strong decrease in MFI especially in higher fiber content biocomposite, is because of strong fiber-fiber interactions.

Moreover, visible fiber breakage during processing likely contributed to higher viscosity (lower MFI), causing increased shear on the fibers. The MFI results indicate that the processability of PLA suffers from the addition of fibers.

Microtomography (µCT)

The purpose of using microtomography in this study was to visualize and analyse the internal structure of the injection molded samples, particularly the distribution and orientation of pulp fibers within the PLA matrix.

The µCT results for PLA-BSWPF and PLA-UBSWPF are presented in Fig. 3. Higher fiber content PLA-BSWPF and PLA-UBSWPF resulted in more agglomeration and void formation, as indicated with arrows in Fig. 3. In PLA 20B and PLA 20UB, more fiber agglomeration was observed, while in PLA 25B and PLA 25UB both fiber agglomeration and void formation was observed.

Void formation visible in Fig. 3 in PLA-BSWPF and PLA-UBSWPF in higher fiber concentrations may have resulted from moisture absorbed by fibers from the environment. Despite the drying step in prior processing, some moisture can remain in the fibers because it is deeply embedded in the cellulose, making it hard to remove with standard drying methods (Chen *et al.* 2022; Zou *et al.* 2023). While injection molding and extrusion help reduce moisture absorption, the moisture already inside the fibers can persist.

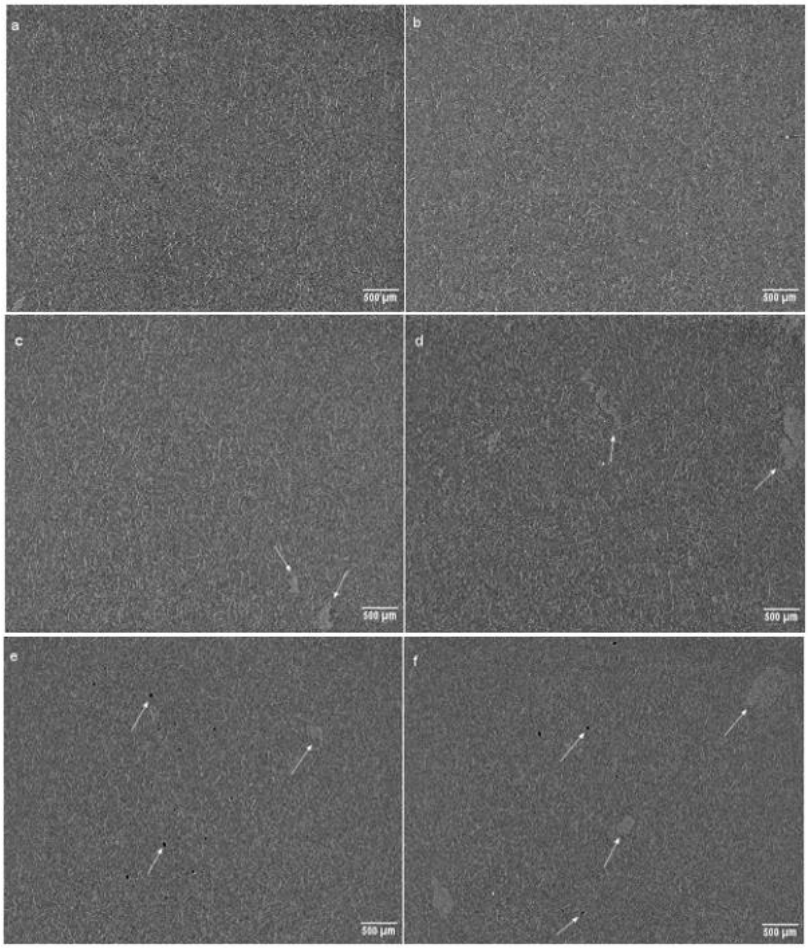

Fig. 3. The X-ray tomography images of PLA 10B (a), PLA 10UB(b), PLA 20B (c), PLA 20UB (d), PLA 25B (e), and PLA 25UB (f); Arrows indicate the fiber agglomerates and voids.

Furthermore, the results in Fig. 2 show that the MFI of higher fiber content PLA biocomposite drastically decreased due to increased melt viscosity. The increased melt viscosity potentially caused void formation and agglomerates due to the reduced mobility within the viscous melt, resulting in poor fiber-fiber interaction.

SEM

Figure 4 shows SEM images of fracture surfaces of PLA 25B and PLA 25UB biocomposites. Small magnification images Fig. 4a and 4c reveal a porous surface, which is common in polymer composites.

Figure 4(d) demonstrates that the PLA 25UB had relatively better polymer-fiber adhesion, while Fig. 4(b) displays opening-up of bleached fibers, *i.e.*, fibrillation. This structural difference can be attributed to the absence of lignin in the bleached fiber (Peltola *et al.* 2019). Increased fibrillation in PLA-BSWPF resulted in higher surface area of the fibers in contact with polymer matrix, which should improve polymer-fiber adhesion. In contrast, PLA-UBSWPF biocomposites showed less fibrillation because lignin provides the binding mechanism for fibers. Although PLA-UBSWPF does not show much fibrillation or fiber breakage, however, visually PLA-UBSWPF showed better polymer-fiber interfaces compared to PLA-BSWPF.

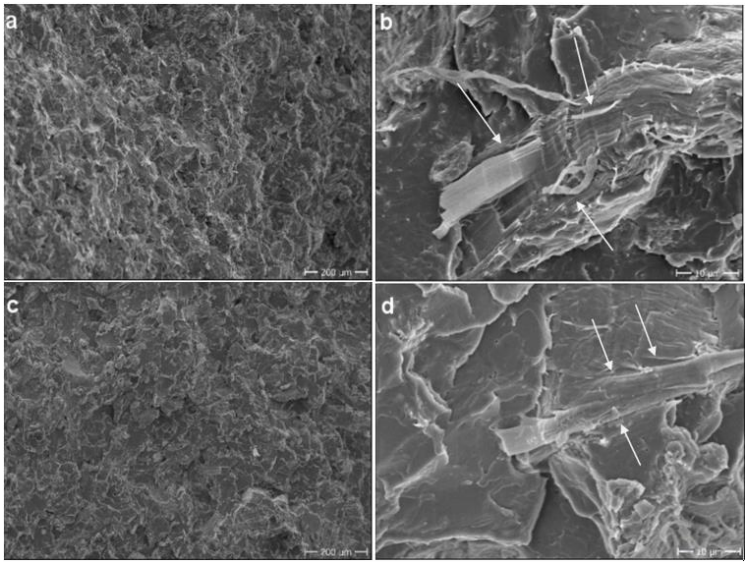

Fig. 4. The SEM images of PLA 25B (a-b) and PLA 25UB (c-d) fracture surfaces

Charpy Impact Strength

Figure 5 illustrates the impact strength of PLA biocomposites with increasing BSWPF and UBSWPF content. PLA-BSWPF showed consistent strength improvement as fiber content increased. PLA 10B experienced a marginal increase of about 3.0%, while PLA 20B and PLA 25B impact strength improved 8.9%% and 9.5%, respectively, compared to neat PLA.

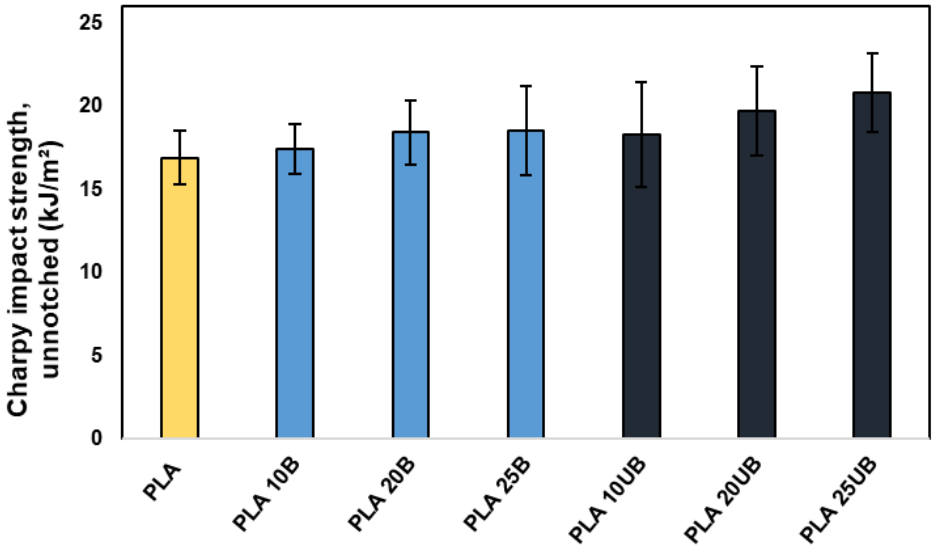

Fig. 5. The Charpy impact strength (unnotched samples) of neat PLA and PLA-BSWPF and PLA-UBSWPF biocomposites

For PLA-UBSWPF biocomposites, a similar trend was apparent; PLA 20UB and PLA 25UB impact strength increased 16.6% and 23.1%, respectively. The relatively better impact strength of PLA-UBSWPF biocomposites can be attributed to better toughness of unbleached fibers containing lignin (Neagu et al. 2006). Furthermore, in Fig. 4 the SEM

images show better polymer-fiber interface in PLA-UBSWPF, which aligns with improved impact strength.

Differential Scanning Calorimetry

Table 2 shows the DSC results for PLA-BSWPF and PLA-UBSWPF biocomposites. Both fiber types improved the degree of crystallinity of PLA biocomposites and showed an increasing trend with increased fiber content. The fibers provided nucleation sites, promoting PLA molecules to align and form a more structured crystalline arrangement (Shazleen *et al*. 2021). The higher crystallinity in PLA-UBSWPF correlates with improved impact results of PLA-UBSWPF in Fig. 5. In general, the addition of BSWPF and UBSWPF to PLA increased the T_g because the fibers restrict the movement of the polymer chains. The T_c decreased because the fibers provided nucleation sites for crystallization to start at lower temperatures.

Table 2. The DSC Results of Neat PLA and PLA-BSWPF and PLA-UBSWPF Biocomposites

Sample	T_g (°C)	T_c (°C)	ΔHc (J/g)	T_m (°C)	ΔH_m (J/g)	Degree of Crystallization (%)
PLA	60.4	100.3	23.41	169.8	37.1	14.63
PLA 10B	62.1	100.5	24.37	168.9	39.3	15.95
PLA 20B	63.1	98.6	15.86	168.5	34.62	20.04
PLA 25B	62.2	96.3	16.20	168.6	39.22	24.59
PLA 10UB	62.6	100.3	23.40	169.3	42.74	15.95
PLA 20UB	63.5	98.4	18.45	168	44.81	28.16
PLA 25UB	63.1	96.6	26.82	167.9	57.40	32.67

Young's Modulus

Figure 6 represents the Young's modulus of PLA, PLA-BSWPF, and PLA-UBSWPF biocomposites.

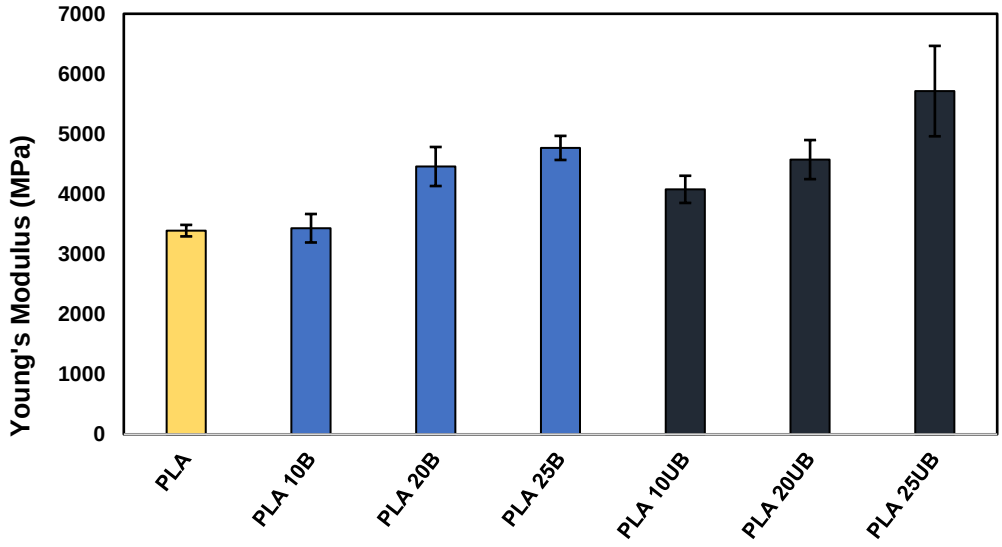

Fig. 6. The Young's modulus of neat PLA and PLA-BSWPF and PLA-UBSWPF biocomposites

The graph shows that both BSWPF and UBSWPF, when added to the PLA matrix, exhibited linear increasing trend in modulus values. For PLA 10B, the modulus increased moderately. However, PLA 20B and PLA 25B showed a noticeable increase in modulus with the highest 40.6% increase in PLA 25B. These results are aligned with the previous research where flexural and modulus strength of PLA-BSWPF was studied with the idea to replace glass fiber reinforced polypropylene with a biocomposite (Delgado *et al.* 2017; Tarrés *et al.* 2019). PLA UBSWPF showed better values of modulus than PLA BSWPF. PLA 25UB modulus increased 68.5% compared to neat PLA. There has been research that shows that lignin improves the modulus of PLA (Esakkimuthu *et al*. 2024; Makri *et al*. 2022), although it should be noted that in these studies lignin is added as reinforcement rather than being incorporated as part of the cellulose fiber. However, the lignin content of the unbleached fibers could contribute to the improved modulus of PLA 25UB.

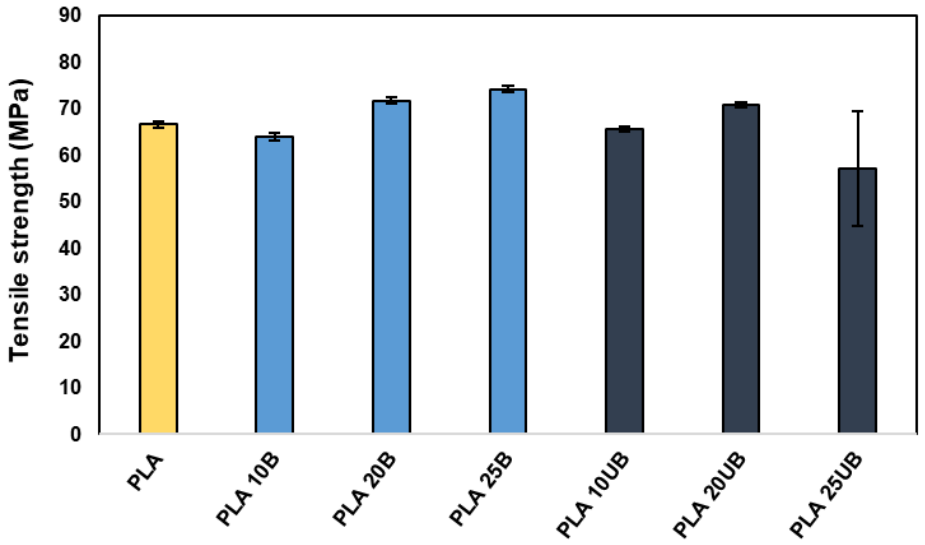

Fig. 7. The tensile strength of neat PLA and PLA-BSWPF and PLA-UBSWPF biocomposites

Tensile Strength

Figure 7 represents the tensile strength of PLA, PLA-BSWPF, and PLA-UBSWPF biocomposites that showed a different trend compared to impact and modulus results. PLA 10B and PLA 10UB tensile strengths showed a slight decrease compared to neat PLA. Instead, PLA 20B and PLA 25B tensile strength increased 7.8% and 11.5% compared to neat PLA. In general PLA-BSWPF showed better tensile results compared to PLA-UBSWPF. SEM results in Fig. 4 showed that PLA-BSWPF had greater fibrillation compared to PLA-UBSWPF, which provides a larger surface area for polymer-fiber contact and potentially allows mechanical interlocking leading to improved tensile strength.

PLA 10UB showed almost similar tensile strength compared to neat PLA. PLA 20UB tensile strength increased 6.4% while PLA 25UB tensile strength drastically decreased 14.2%. This sudden decrease in tensile strength of PLA 25UB can be attributed to agglomeration and void formation visible in the µCT images in Fig. 3f. The higher standard deviation in PLA 25UB indicates sample variability attributed to the presence of more voids and agglomerations within the biocomposite, which in turn elucidates the reduced tensile strength.

CONCLUSIONS

1. The composite of poly(lactic acid) and bleached softwood pulp fibers (PLA-BSWPF) exhibited higher fibrillation compared to PLA-UBSWPF.
2. The composite with unbleached kraft fibers (PLA-UBSWPF) showed higher degree of crystallization compared to PLA-BSWPF.
3. PLA-UBSWPF exhibited higher modulus and impact strength compared to PLA-BSWPF, while PLA-BSWPF showed higher tensile strength.
4. Higher fiber content PLA biocomposites showed void formation and agglomeration of fibers.

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