

Waste-derived natural fillers in poly(3-hydroxybutyrate-co-3-hydroxyvalerate)-based biocomposites for short-lifespan products: A route toward fully compostable materials

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ABSTRACT

The growing demand for sustainable materials has driven interest in polyhydroxyalkanoates (PHAs), such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), which are biodegradable alternatives to conventional plastics. The inherent brittleness of PHBV limits its applications. To address this, natural waste-derived fillers, such as walnut shell (WS), cellulose (CEL), and wood filler (WF) were incorporated into PHBV matrices to enhance their mechanical and functional properties. The study investigated the impact of these fillers on PHBV composites, considering the mechanical performance of the developed composites and their hydrolytic degradation behaviour in a biologically active environment. The results indicated that the type and concentration of filler significantly influenced the material's performance. In general, the incorporation of fillers led to an increase in stiffness, accompanied by a reduction in tensile strength. The most pronounced changes were observed for the composites containing CEL and WF, while less significant effects were noted for WS. The incorporation of 7.5 wt.% fillers altered the degradation behaviour of the mechanical properties, which was particularly evident in the case of the modulus. Degradation resulted in an overall decrease in mechanical performance, especially in tensile strength (by up to ~20%) and elastic modulus, with more pronounced effects in filler-reinforced composites compared to unmodified PHBV. In contrast, flexural strength exhibited relatively smaller changes, suggesting a partial preservation of structural integrity despite the progressing material degradation. This study underscored the potential of natural fillers for enhancing the sustainability and performance of PHBV composites, demonstrating their suitability for short-lifespan, compostable applications. These findings contribute to the development of fully biodegradable materials in line with circular economy principles, highlighting the importance of optimising filler-matrix interactions for real-world applications.

Keywords: hydrolytic degradation, circular economy, walnut shell powder, cellulose, wood filler, polyhydroxyalkanoates.

INTRODUCTION

The need for sustainable materials has led to a growing interest in biodegradable polymers, such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), which offer an environmentally

friendly alternative to conventional petroleum-based plastics (El-Taweel and Al-Hamdi, 2024). The inherent brittleness of PHBV limits its applications requiring high mechanical performance, particularly in areas like packaging and agriculture. To address this issue, researchers have

focused on reinforcing PHBV with natural fillers derived from renewable resources, which not only enhance the mechanical properties of PHBV, but also contribute to the development of fully compostable materials.

Ground walnut shell (WS), a waste product from the food industry, is a lightweight, renewable filler that has gained attention in biopolymer composite research. WSs are rich in lignin and cellulose, providing both structural reinforcement and improved dimensional stability to PHBV. Li et al. (2024) demonstrated that incorporating delignified bamboo fibre (DBF) and WS powder into a melamine-hexamethylenediamine-urea (MHU) resin significantly enhanced the mechanical properties of hybrid composites, achieving flexural strength up to 220 MPa and tensile strength of 120 MPa, surpassing conventional composites. The composites also exhibited high flame retardancy, reaching a UL 94-V0 rating, and showed unexpected fluorescence under UV light, providing potential use in security marking and authentication technologies. WS also enhances the surface properties of the composite, making it suitable for applications in packaging and agricultural products (Mandala et al., 2023). However, like wood filler (WF), WS presents challenges related to filler-matrix compatibility, heat resistance, and the need for optimisation in terms of particle size and filler concentration.

Cellulose (CEL) is one of the most studied natural fillers, known for its high strength, renewability, and biodegradability (Nishino et al., 2004). CEL fibres have been shown to improve the mechanical performance of PHBV composites significantly. For example, Meereboer et al. (2020) found that blending PHBV with plasticized cellulose acetate (pCA) improved the impact strength, particularly with higher pCA contents, while reducing crystallinity and density. The addition of triethyl citrate (TEC) as a plasticiser facilitated partial plasticisation of PHBV, lowering its melt temperature and creating secondary crystallites. However, phase separation remained evident in the blends, while the chain extender exerted only a limited effect on tensile strength and Young's modulus. Uniform dispersion of CEL fibres in the PHBV matrix also remained challenging due to fibre agglomeration during processing, resulting in structural heterogeneity and reduced mechanical performance (Khoshkava and Kamal, 2014; Pandey et al., 2013).

WF, another widely used natural filler, is a low-cost, renewable material that is rich in cellulose and hemicellulose. It has been successfully incorporated into PHBV composites to enhance their mechanical properties, particularly stiffness and flexural strength (Karmarkar et al., 2007; Kuciel and Liber-Kneć, 2011; Schirp and Stender, 2010). Chan et al. (2018) found that incorporating maleic anhydride-grafted PHBV into WF composites improved their tensile strength and impact strength, although the improvements were modest. The use of pMDI (polymethylene diphenyl diisocyanate) enhanced the tensile strength by 25%, but at higher concentrations, it led to a decline in strength and strain at break due to void formation. The study also demonstrated that processing conditions, particularly extrusion shear, had a significant effect on the mechanical properties, with higher shear leading to substantial degradation in performance. WF also helps reduce the overall cost of the composite, as it is a by-product of the wood industry. The main challenge with WF is the potential for poor compatibility with the polymer matrix, as the hydrophilic nature of WF often leads to weak interfacial bonding between the filler and PHBV (Norouzpour et al., 2022; Xie et al., 2025). Surface modifications or the use of coupling agents are typically employed to improve filler-matrix interaction and enhance composite performance, but this procedure may increase production cost and processing time.

Although research on natural fillers in PHBV composites is abundant, one critical aspect often overlooked is how these materials behave under real environmental conditions. Specifically, the hydrolytic degradation of PHBV composites, especially when exposed to elevated temperatures and aggressive environments, has not yet been extensively studied. A novel approach in this research involves exposing PHBV composites to the water enriched with septic tank treatment agents, simulating real-world, biologically active environments such as wastewater or composting systems. This method subjects the composites to both elevated temperatures and active microbial cultures, offering valuable insights into their degradation behaviour. This study provides new insight into the hydrolytic degradation of composites with WS, CEL, and WF, providing crucial information on the longevity and performance of these materials in environments that closely mimic real disposal scenarios. The novelty lies in using this realistic degradation model, offering an

innovative approach to understanding how biocomposites will perform over time, how they will degrade, and how their final disposal will occur in aggressive, biologically active environments. This type of research is critical for assessing the suitability of these biocomposites for short-lifespan, fully compostable products, and understanding the full degradation process is vital for developing truly sustainable materials that can replace conventional plastics in industrial applications.

In conclusion, this study represents a novel approach to evaluating PHBV-based biocomposites by investigating the hydrolytic degradation in aggressive environments, particularly using septic tank treatments as a model for biodegradation. Such studies are necessary for determining the lifespan of these materials under real-world conditions and for improving the overall sustainability of biodegradable composites by ensuring that their degradation is both effective and environmentally friendly.

MATERIALS AND METHODS

Composites manufacturing

The polymer matrix used for the preparation of the composites was poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), a member of the polyhydroxyalkanoates (PHAs) family. PHBV is a biodegradable and bio-based thermoplastic copolymer synthesised through bacterial fermentation. It consists of repeating units of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV), with the latter imparting increased flexibility and processability compared to neat polyhydroxybutyrate (PHB) (Witko et al., 2018). Due to its bio-origin and full compostability under industrial conditions, PHBV is considered one of the most promising green alternatives to conventional petroleum-derived polymers. In this study, PHBV (PHI 002) purchased from Nature Plast (France) was used as a matrix. It is a 100% biodegradable polymer with the following properties: density – 1.25 g/cm³, fluidity index –190 °C/2.16 kg – 15–30 g/10 min, tensile modulus – 4 500 MPa, Charpy impact test (without notch) – 5 kJ/m² and thermal resistance (HDT B) – 134 °C.

To improve the mechanical properties and sustainability profile of the biopolymer, three types of natural waste-derived fillers (J. Rettenmaier &

Söhne GmbH, Rosenberg, Baden-Württemberg, Germany), were incorporated:

- Ground walnut shell (REHOFIX Walnut 200): A lignocellulosic agricultural waste product rich in hemicellulose and lignin, offering moderate stiffness and low density. Its use in composites provides an eco-friendly valorisation route for food processing residues. Fillers with a particle size ranging from 100 µm to 200 µm were used. It has a bulk density between 400 g/l and 700 g/l, a pH value of 4.5 to 7.0, and a low oxide ash content (~1%), making it suitable for various applications in composite materials. WSs are lignin-rich (~35 wt.%) with ~30 wt.% cellulose and ~25 wt.% hemicellulose (dry basis). In authors' previous study, SEM micrographs revealed that walnut shell particles exhibited an irregular, angular morphology with a rough surface texture rather than a well-defined fibrous structure (Bazan et al., 2021).
- Microcrystalline cellulose (ARBOCEL®, EFC950): A refined form of cellulose obtained from plant biomass through acid hydrolysis, offering a high surface area and reinforcing potential due to its semicrystalline structure and fibrous morphology. Cellulose is known for its stiffness, renewability, and compatibility with biopolymer matrices. It is a light yellow cellulose powder made from chemithermomechanical pulp. It has a bulk density of 170–240 g/l with the main particle size falling between 70 and 200 µm. The particle diameter typically ranges from 10 µm to 50 µm, giving them a fine, irregular structure. The composition includes 85–90 wt.% cellulose, 5–10 wt.% lignin, and 5–7 wt.% hemicellulose. The cellulose fillers were characterised by elongated, particle-like morphologies with relatively high aspect ratios, irregular dimensions, and heterogeneous filler size distribution, which are characteristic features of chemithermomechanical pulp-derived lignocellulosic reinforcements (Doineau et al., 2022).
- Wood filler (C100): A fine particulate by-product of the wood industry, composed primarily of lignocellulosic material. It serves as a low-cost, abundant filler that contributes to increased rigidity while maintaining the biodegradability of the composite. The main particle range is 70–150 µm and particle diameters from 10 to 50 µm, giving it a fine, irregular structure. The composition consists of approx. 85–90 wt.%

cellulose, 5–10 wt.% lignin, and 5–7 wt.%. Wood filler particles were described as irregular lignocellulosic particles with heterogeneous geometry and varying aspect ratios depending on the particle size fraction. Microscopic observations revealed angular and partially elongated structures characteristic of mechanically milled wood filler (Siwek et al., 2018).

The PHBV granules provided by Nature Plast (Mondeville, France) and filler powders were weighed and mixed according to predefined weight percentages. Each filler was added to the polymer matrix at two concentrations: 7.5 wt.% and 15 wt.%. Before processing, PHBV pellets were dried in a molecular dryer DRYMAX primus E30-70-M molecular dryer (Vienna, Austria) at 40 °C for 4 h to achieve max. humidity of 0.025%.

Subsequently, fillers were dried in an oven at 80 °C for 48 h. PHBV and particles were compounded using a co-rotating twin-screw extruder (Maris America Corp., Windsor Mill, MD, USA). Finally, standard dumbbell samples were injection moulded by using the KM 40–125 Winner Krauss Maffei, Krauss Maffei injection moulding machine (Munich, Germany) according to the PN-EN ISO:3167 standard with dimensions $10 \times 4 \times 150$. The injection process parameters were respectively: moulding zones: 140 °C, 160 °C, 165 °C and 170 °C. The screw rotational speed was 50 rpm, the screw recovery distance was 50 mm, and the applied back pressure was 85 bar. The injection pressure and holding pressure were set to 500 bar and 100 bar, respectively, with a holding distance of 8 mm. Table 1 presents the composite formulations and their densities (Figure 1).

Table 1. Sample designation and composites density

Composite formulation	Abbreviation	Density, g/cm ³
Neat poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	PHBV	1.26
PHBV with 7.5 wt.% walnut shell filler	PHBV/WS7.5	1.26
PHBV with 15 wt.% walnut shell filler	PHBV/WS15	1.28
PHBV with 7.5 wt.% cellulose filler	PHBV/CEL7.5	1.26
PHBV with 15 wt.% cellulose filler	PHBV/CEL15	1.27
PHBV with 7.5 wt.% wood filler	PHBV/WF7.5	1.26
PHBV with 15 wt.% wood filler	PHBV/WF15	1.27

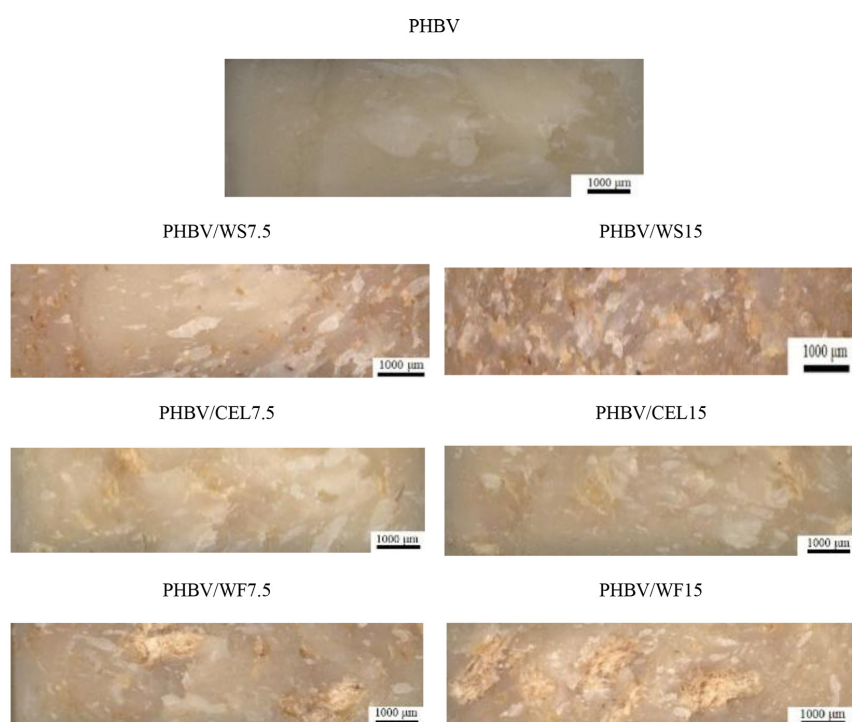


Figure 1. Optical images of PHBV and its composites

Methods

Optical images

Optical microscopy was employed to examine the surface morphology and fracture characteristics of the specimens after tensile testing. Observations were carried out using a digital optical microscope Keyence VHX series (Keyence Corporation, Osaka, Japan). Images were captured in reflected light mode under varying magnifications (typically ranging from $\times 20$ to $\times 50$), depending on the scale and nature of the observed features.

All micrographs were acquired under identical and predefined imaging parameters to ensure that the microscope and software setup did not influence the observed differences between samples using the integrated imaging software; all measurements were conducted using software provided by the microscope manufacturer.

Mechanical tests

Mechanical properties were evaluated through a series of standardised tests. Uniaxial tensile tests were carried out in accordance with ISO 527 (ISO 527-1:2019 – Plastics — Determination of Tensile Properties — Part 1: General Principles, n.d.), utilising a Shimadzu AGS-X universal testing machine (10 kN capacity, Kyoto, Japan). A constant crosshead speed of 5 mm/min was applied, and an axial extensometer was employed to ensure accurate strain measurements. Initial mechanical hysteresis loops were also recorded under the same setup. Standard dumbbell samples with dimensions $10 \times 4 \times 150$ were used.

Flexural behaviour was assessed following ISO 178 (ISO 178:2019 – Plastics — Determination of Flexural Properties, n.d.) using an MTS Criterion 43 universal testing system (Minnesota, USA) equipped with TestSuites 1.0 software. The tests were performed at a crosshead speed of 10 mm/min, employing a 3 kN load cell and a support span of 80 mm in a three-point bending configuration. Standard beam shape samples with dimensions 10×4 were used.

Impact strength was measured according to ISO 179 (ISO 179-1:2010 – Plastics — Determination of Charpy Impact Properties — Part 1: Non-Instrumented Impact Test, n.d.) using a Zwick/Roell MTS-SP impact tester (Ulm, Germany). Charpy impact tests were conducted on

unnotched specimens with an applied energy of 5 J. Standard beam shape samples with dimensions 10×4 without a notch were used. In composites with natural fillers, notches expose the filler surface and facilitate crack initiation, resulting in lower impact strength.

All reported values represent the mean results obtained from a minimum of five individual specimens for each test condition. Sensitivity class 0.5.

Hydrolytic degradation

To assess the environmental durability of the fabricated composites, a hydrolytic degradation study was conducted over a period of 30 days. The objective was to evaluate both the water absorption behaviour and the extent of material deterioration under aggressive aqueous conditions simulating real-life biodegradation scenarios (modified ISO 62 standard (Iso, 2008)).

The specimens were immersed in an aqueous solution maintained at 40 °C, consisting of a commercially available septic system treatment. This formulation contained citric acid, subtilisin (a proteolytic enzyme), amylase, and a mixture of bacterial cultures, designed to mimic biologically active and enzymatically rich environments typically found in wastewater or septic systems. Bacteria + Trichoderma 400 g EKOKOMPOST™ is a 100% organic, microbiological fertiliser. It contains natural strains of bacteria and Trichoderma spp. fungi, which specialise in composting even difficult-to-decompose organic waste, such as leaves and pine needles. The recommended dose is 1g per 1 litre of aqueous solution. During the experiment, the samples accounted for 5 vol.% of the solution, and the solution was replenished weekly to compensate for evaporation losses. The pH was monitored and remained in the range of 7.0–7.5 throughout the test, and neat PHBV was used as a blank control sample.

Water uptake was monitored throughout the degradation process. The samples were dried with paper and weighed immediately after removal from the solution. Mass measurements were recorded every 2 days during the first week and then every 7 days thereafter, up to the 30th day. A precision analytical balance (Ohaus Adventurer, Parsippany, NJ, USA) was used for weighing, and the percentage of water absorption (M_t) was calculated using Equation 1:

$$M_t = \left[\frac{W_t - W_0}{W_0} \right] \times 100 \quad (1)$$

where: M_t – percentage of water content;
 W_t – instantaneous weight of the sample;
 W_0 – the initial weight of the sample.

Upon completion of the 30-day degradation period, the specimens were removed from the solution, dried by paper, and subjected to mechanical testing. Both tensile and flexural tests were performed in accordance with standard protocols to evaluate the residual mechanical integrity of the composites after prolonged hydrolytic exposure.

RESULTS AND DISCUSSION

Mechanical properties

PHBV is a biodegradable thermoplastic polyester the intrinsic brittleness and low impact resistance of which significantly limit its structural applications, despite its excellent biocompatibility and environmental profile (Jost and Langowski, 2015). Reinforcement with lignocellulosic fillers, such as ground walnut WS, CEL, or WF, represents a promising route to tailor its mechanical performance while maintaining full biodegradability. Each of these fillers differs in chemical

composition, morphology, and interfacial adhesion potential, which profoundly influences stress transfer efficiency as well as fracture mechanisms under tensile and flexural loading. Tensile tests provide insights into filler-induced modifications of the elastic modulus, yield strength, and ductility, enabling evaluation of the extent to which the reinforcing phase constrains or promotes polymer chain mobility. In contrast, flexural tests assess the resistance of the composite to bending-induced stresses, where both tensile and compressive failure modes interact, often revealing different sensitivity to filler geometry and dispersion. CEL particles, with their high aspect ratio and crystallinity, are generally reported to enhance stiffness and tensile strength through effective load-bearing, while WF may act as a moderately reinforcing but more isotropic phase due to its heterogeneous particle shape (Venkatarajan et al., 2021). WS, containing lignin and phenolic components, may introduce additional stiffening but also stress concentration areas, potentially lowering strain-to-failure under uniaxial tension yet improving resistance to surface indentation under bending (Pradhan and Satapathy, 2022). Differences in filler–matrix interfacial adhesion will manifest distinctly in tensile versus flexural responses, as poor bonding typically reduces tensile strength more severely than flexural strength due to the latter’s tolerance to

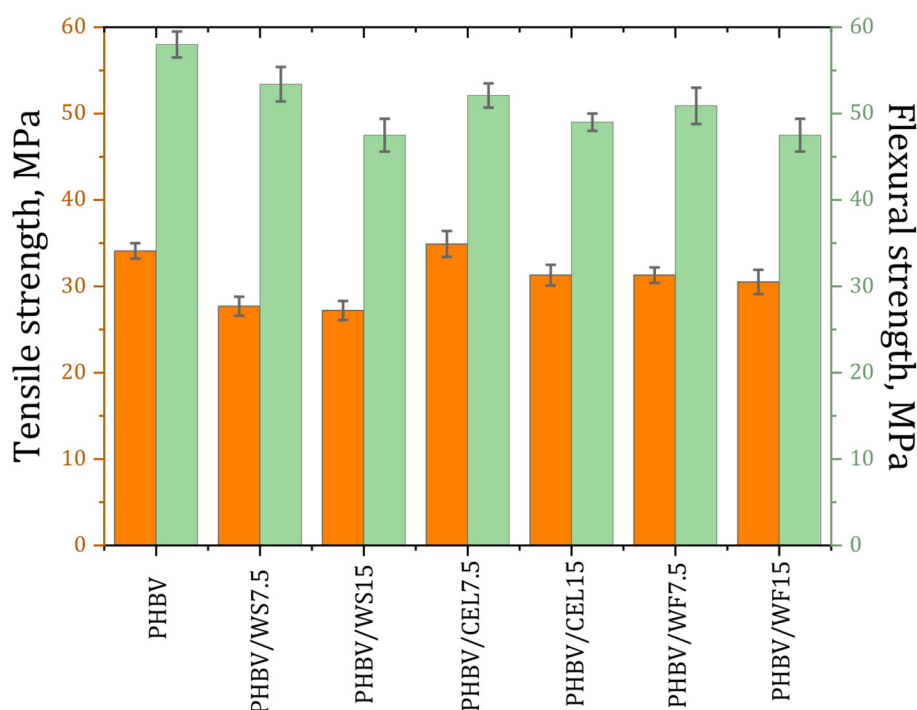


Figure 2. Tensile and flexural strength of PHBV and its composites

localised debonding. By systematically comparing tensile and flexural performance, the present study aimed to elucidate the interplay between filler morphology, interfacial phenomena, and load transfer mechanisms in PHBV-based composites. Such an understanding is critical for optimising bio-based polymer composites for load-bearing applications while aligning with the principles of sustainable materials engineering.

Mechanical properties (tensile strength, flexural strength, Young's modulus and flexural modulus) of PHBV and its composites were summarised in Figures 2 and 3. The introduction of lignocellulosic fillers into the PHBV matrix significantly changed its mechanical properties, with both the type of filler and its mass fraction having a decisive influence. Mechanical characterisation revealed clear trends depending on filler type and loading level. These trends reflected differences in reinforcement mechanisms and interfacial interactions. In tensile testing, WS consistently reduced the tensile strength compared to neat PHBV, at both 7.5 wt.% and 15 wt.%, while producing negligible changes in Young's modulus. The absence of a significant stiffening effect can be attributed to the particulate, low-aspect-ratio morphology of WS and its limited surface polarity, which result in poor mechanical and physicochemical coupling with the PHBV matrix (Kuciel et al., 2019). The ANOVA results confirmed a significant reduction

in tensile strength for the WS-filled composites ($p < 0.05$). In contrast, CEL and WF imparted a pronounced stiffening effect, with increases in Young's modulus of up to $\sim 30\%$, attributable to their high aspect ratio, inherent stiffness, and ability to form load-bearing networks aligned with the flow direction during melt processing (Jose et al., 2025). However, these gains in stiffness were accompanied by reductions in tensile strength particularly at 15 wt.% indicative of filler agglomeration, poor wetting, micro-void formation, and dominant failure modes such as debonding and filler pull-out (Mehdikhani et al., 2019). The ANOVA analysis highlighted that the decrease in tensile strength at 15 wt.% CEL and WF was statistically significant ($p < 0.05$).

Under flexural loading, all fillers led to a reduction in flexural strength, while the variations in flexural modulus were less straightforward compared to those observed in the tensile test. WS produced an increase in flexural modulus ($+8\text{--}9\%$), suggesting an efficient particle packing effect and improved constraint of local deformations in bending. Conversely, CEL and WF reduced the flexural modulus by $4\text{--}9\%$, which can be linked to the dual stress state in bending tensile on one face and compressive on the other, where filler micro-buckling and interfacial debonding are more likely to occur in the compressive zone (Jiang et al., 2021). ANOVA results indicated that the flexural

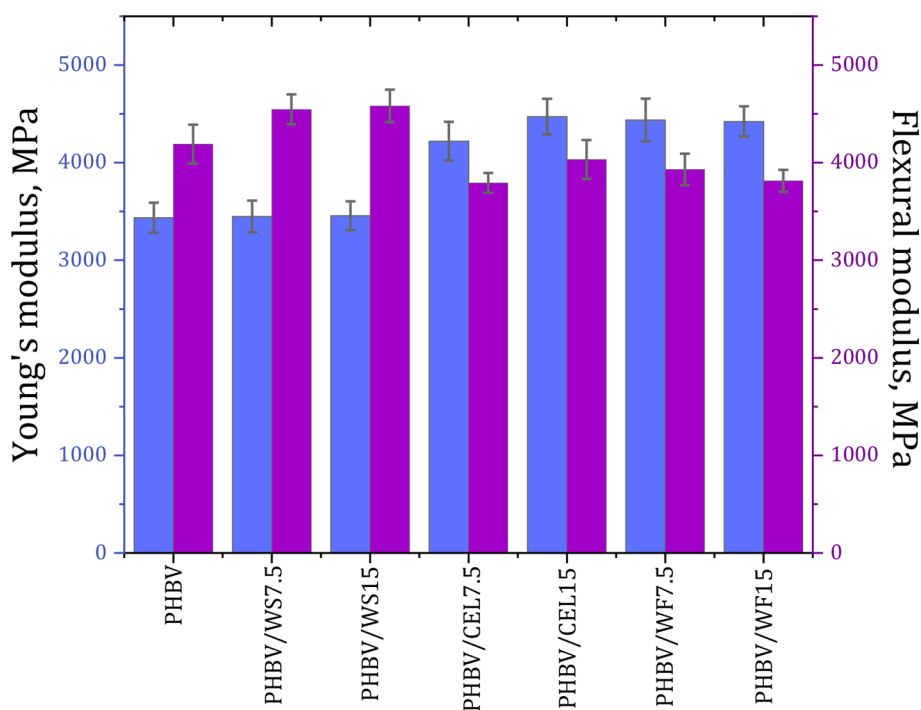


Figure 3. Young's and flexural modulus of PHBV and its composites

modulus differences were also statistically significant ($p < 0.05$), supporting the observation that the changes in modulus are relatively small compared to those in tensile properties.

Increasing the filler content from 7.5 wt.% to 15 wt.% generally exacerbated brittleness and reduced strength in both tensile and flexural modes, in agreement with previous reports on lignocellulosic-reinforced biopolyesters (Bledzki and Jaszkiwicz, 2010). This behaviour is driven by: (i) higher stress concentration at particle–matrix interfaces, (ii) restricted chain segment mobility in PHBV, (iii) a greater probability of defect formation (micro-cracks, voids), and (iv) a pronounced decrease in toughness and elongation at break. As such, for fillers, there is a clear trade-off between stiffness and strength, whereas for fine particulates, tensile properties remain largely unaffected, but modest flexural stiffening can be observed.

The comparative analysis between tensile and flexural behaviour underscores the critical role of filler orientation, load transfer pathways, and damage mechanisms. In tension, oriented fillers form effective load-bearing skeletons, leading to modulus enhancement with CEL and WF. In bending, the compressive side is prone to filler kinking, microbuckling, and debonding, which limit reinforcement efficiency. This divergence in mechanical response points to the necessity of improving interfacial adhesion through surface modification or coupling agents such as diisocyanates, Joncryl®, or TGIC to suppress filler pull-out, enhance matrix wetting, and preserve structural integrity (Sanchez-Safont et al., 2021).

Overall, the obtained results reveal two dominant reinforcement trends: (i) lignocellulosic particles (CEL, WF) significantly stiffen PHBV under tensile loading but are less effective or even detrimental under flexural loading; (ii) fine-particle fillers (WS) have negligible tensile benefits but can modestly increase flexural modulus. In both cases, higher filler concentrations amplify the negative effects on strength, which aligns with the literature consensus for lignocellulosic-reinforced PHBV systems.

Impact properties

Impact strength is a critical property in the design and application of thermoplastic polymer composites, particularly when these materials are subjected to sudden or dynamic loading conditions. The Charpy impact test provides a reliable

measure of a material's ability to absorb and dissipate energy during rapid fracture. This parameter is especially relevant for engineering components where accidental impacts, drops, or cyclic shock loads may occur during service (Jogur et al., 2018).

From a micromechanical perspective, impact fracture in thermoplastic composites involves several energy dissipation mechanisms, including matrix yielding, shear band formation, filler/matrix interfacial debonding, filler pull-out, filler fracture, and crack deflection. In unreinforced thermoplastics, energy absorption is dominated by plastic deformation of the polymer matrix and the development of crazes or shear yielding zones. In filler-reinforced systems, additional mechanisms such as interfacial crack propagation and filler bridging contribute significantly to the overall impact resistance. The effectiveness of these mechanisms depends strongly on the quality of interfacial adhesion and the inherent toughness of both the polymer and the reinforcement phase.

Incorporation of lignocellulosic particles, such as WF, hemp shives, flax fibres, or other plant-derived fillers, introduces specific effects that can influence impact performance (Schirp and Stender, 2010). Due to their hydrophilic nature and relatively low intrinsic toughness compared to synthetic fibres, lignocellulosic reinforcements may induce stress concentrations at the particle/matrix interface, especially if interfacial adhesion is insufficient. This can promote premature crack initiation and reduce impact strength. On the other hand, if the filler–matrix adhesion is optimised (e.g., via compatibilisation, coupling agents, or surface treatments), lignocellulosic fillers can contribute to crack path tortuosity, enhance energy absorption through filler pull-out, and delay catastrophic fracture. Moreover, the elongated morphology of certain natural fillers can support load transfer and inhibit rapid crack propagation.

The influence of lignocellulosic particles on impact strength is therefore governed by a balance between stiffening effects, interfacial bonding, and the capacity of the reinforcement to contribute to post-crack energy dissipation. High filler content, poor dispersion, and weak bonding tend to embrittle the composite, whereas moderate loading levels, good dispersion, and tailored interface chemistry can maintain or even improve toughness relative to the neat polymer (Zhang et al., 2017).

The Charpy impact test remains an essential tool for the mechanical characterisation of thermoplastic composites because it captures the

synergistic effects of matrix ductility, reinforcement morphology, and interfacial properties under high strain-rate conditions. The results provide valuable insight into the material's failure behaviour, enabling optimisation of composite formulations for specific engineering applications where impact resistance is a critical design parameter. In the case of lignocellulosic-reinforced composites, such testing is particularly important for understanding how natural filler characteristics, moisture sensitivity, and processing-induced morphology influence durability and reliability in real-world service environments (Qaiss et al., 2015).

Figure 4 presents the impact strength results obtained from the Charpy test. The incorporation of lignocellulosic fillers: WS, CEL, and WF into the PHBV matrix led to a notable decrease in impact strength compared to the neat polymer (12.0 kJ/m²). This reduction is consistent with previous findings for brittle biopolymers reinforced with stiff, low-deformability phases. The most pronounced reduction was observed for WS, with impact strength decreasing by 28% and 36% for 7.5 wt.% and 15 wt.% loadings, respectively. This can be attributed to the irregular shape and intrinsic brittleness of WS particles, as well as their likely poorer interfacial adhesion, which facilitates early crack initiation. In the case of WF, the impact strength values were similar for both loadings (7.8–8.2 kJ/m²), suggesting that the dominant factor controlling toughness reduction is brittle interfacial fracture, which is largely independent of filler concentration. Conversely, CEL exhibited an atypical trend, with a higher value

recorded for 15 wt.% (9.1 kJ/m²) compared to 7.5 wt.% (8.5 kJ/m²). This improvement can be linked to better dispersion and possible formation of filler-bridging structures at higher loadings, which may delay crack propagation and activate additional energy-dissipation mechanisms.

A one-way ANOVA was performed to assess the significance of the differences between the impact strength of PHBV and its composites. The ANOVA results showed significant differences between the samples ($p < 0.05$). The post-hoc Tukey's HSD test revealed the following results:

WS composites showed a significant reduction in impact strength compared to neat PHBV, with a decrease of 28% and 36% at 7.5 wt.% and 15 wt.%, respectively ($p < 0.05$).

WF composites displayed similar impact strength values (7.8–8.2 kJ/m²) across both 7.5 wt.% and 15 wt.% loadings, indicating no significant effect of filler concentration on impact strength ($p > 0.05$).

CEL composites showed a slight improvement in impact strength at 15 wt.% (9.1 kJ/m²) compared to 7.5 wt.% (8.5 kJ/m²), and this difference was found to be statistically significant ($p < 0.05$).

At the microstructural level, the observed changes can be explained by the synergy of several mechanisms: (i) stress concentration at the filler–matrix interface due to elastic modulus mismatch; (ii) crack initiation and propagation along poorly bonded interfacial regions; (iii) brittle fracture promoted by residual thermal stresses generated during cooling; (iv) fibre pull-out in the case of fibrous

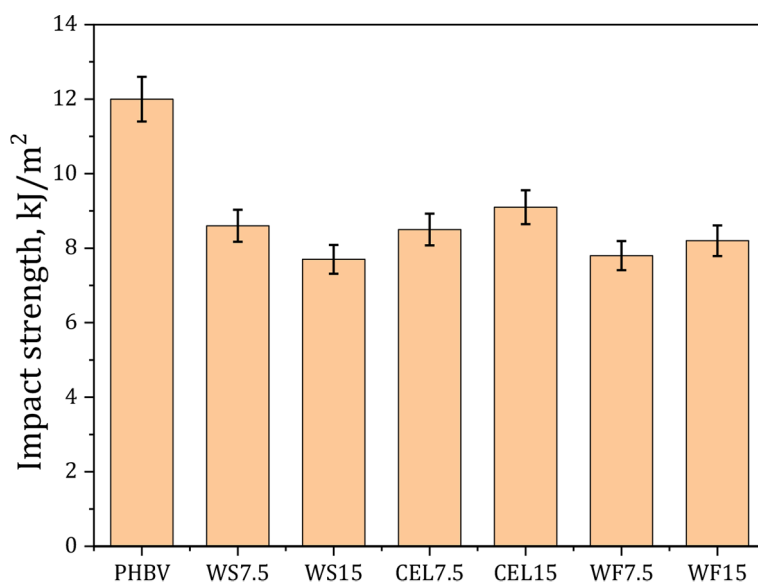


Figure 4. Impact strength of PHBV and its composites

fillers, enabling partial energy absorption; (v) interfacial friction during fibre sliding; and (vi) microfibrillation in cellulose-rich composites, which increases the crack path length. Despite the overall reduction in impact strength, the obtained values (7.7–9.1 kJ/m²) remain sufficient for the applications where dynamic loads are moderate, and the priorities are low density, biodegradability, and renewable origin of the materials. These include rigid reusable packaging, agricultural components, low-impact protective casings, and household equipment with limited exposure to impact events.

The trends observed here are consistent with earlier literature reports. Conceição et al. (Conceição et al., 2023) reported that lignocellulosic fillers tend to act as crack initiators in brittle matrices, reducing the contribution of plastic deformation to energy absorption. According to Naghmouchi et al. (Naghmouchi et al., 2015), increasing filler content generally intensifies stress-concentration effects, although this can be partly offset by filler pull-out and microfibrillation if the interface is sufficiently strong, an effect comparable to that observed for CEL15 in this work. McNeill et al. (McNeill et al., 2024) found that larger particles with irregular morphology, such as WS, cause more severe toughness deterioration compared to fibrous or finer particulate fillers, in agreement with the strong reduction noted here for WS. Moreover, Masłowski et al. (Masłowski et al., 2020) demonstrated that surface modification of lignocellulosic fillers (e.g., silanisation, acetylation) improved the impact strength of the composites, increasing it by approximately 20–40%. This enhancement is mainly attributed to the reduction of premature crack initiation and better stress transfer between the filler and the polymer matrix.

In light of these findings, it can be concluded that the main barrier to improving PHBV/lignocellulose toughness is insufficient interfacial compatibility, particularly for coarse, brittle particulate fillers. The fact that CEL15 showed improved impact strength compared to CEL7.5 suggests that at higher filler loadings, additional energy-dissipation mechanisms such as filler bridging, controlled microcracking, and local matrix plasticisation around filler regions can be activated. This indicates that a balanced strategy involving optimised particle morphology, controlled filler size distribution, and targeted surface modification could shift the stiffness-strength-toughness balance towards a more favourable property profile.

Hydrolytic degradation

The study of hydrolytic degradation in aqueous environments containing septic tank additives is of particular relevance for such composites as it provides critical insight into their long-term stability, structural integrity, and biodegradation behaviour under chemically and biologically active conditions that simulate real disposal or service environments. Septic tank preparations typically contain a complex mixture of enzymes (e.g., cellulases, amylases, lipases, proteases) and microbial consortia (often including *Bacillus* spp. and other hydrolytic bacteria), which can catalyse not only the breakdown of organic waste but also biopolymeric materials. These conditions can simulate a biologically active, nutrient-rich aqueous environment, in which the synergy between hydrolytic enzymes and microorganisms enhances the rate and complexity of PHBV composite degradation. For lignocellulosic-reinforced PHBV, additional degradation phenomena may arise from the preferential enzymatic attack on the carbohydrate-rich fillers, which increases porosity, facilitates water diffusion, and exposes more polymer matrix to hydrolytic scission.

From a materials science perspective, such degradation involves coupled mechanisms: (i) water sorption and swelling, particularly in hydrophilic filler domains; (ii) enzymatic depolymerisation of both filler and matrix, initiated at amorphous regions; (iii) filler matrix interfacial debonding and consequent loss of load-bearing capacity; and (iv) microbial colonisation of exposed surfaces, further promoting localised polymer erosion. Over time, these processes may result in embrittlement, loss of mechanical integrity, and fragmentation into smaller debris, which are subsequently more accessible to biodegrading agents.

Understanding these interactions is critical for predicting the environmental performance and service life of PHBV lignocellulose composites in applications where accidental or deliberate exposure to aqueous microbial environments may occur. In particular, knowledge of degradation kinetics and mechanisms under septic-like conditions can inform material design strategies such as filler selection, surface treatment, or matrix modification aimed at tuning the balance between durability in service and biodegradability post-use.

The results presented in Figures 5a and 5b show the mass change during the hydrolytic degradation of PHBV and its composites over a 30-day

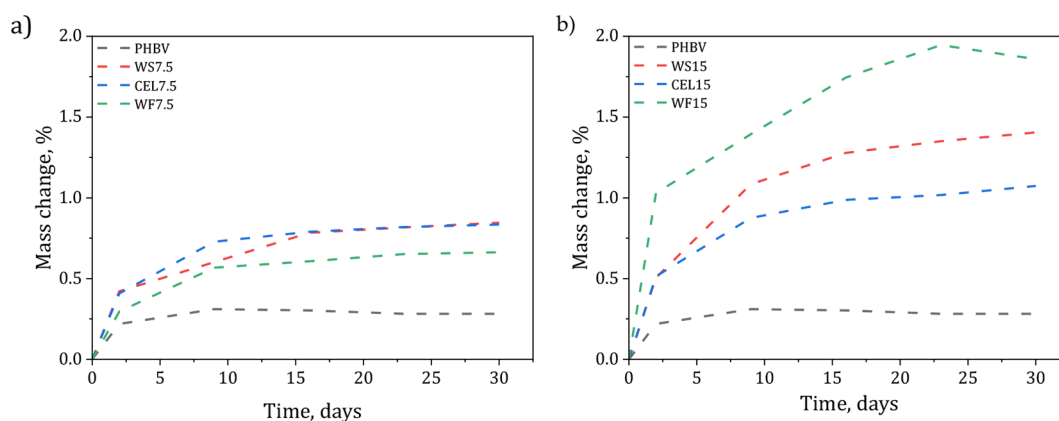


Figure 5. Mass change during hydrolytic degradation of PHBV and its composites

period, indicating the effect of different filler additives on water absorption behaviour. Figure 5a illustrates the mass change for composites with 7.5 wt.% filler content, while Figure 5b displays the mass change for composites with 15 wt.% filler content. Both figures demonstrate a clear trend of increasing mass over time, reflecting water uptake and possible hydrolytic degradation, which is typical for biodegradable materials like PHBV (Deroine et al., 2014). However, significant differences in water uptake can be observed between the different composite formulations. In both figures, neat PHBV exhibits the lowest water absorption rate, reaching approx. 0.25–0.30%, showing a gradual increase in mass, which stabilises after approx. 5 days. This indicates that the neat polymer, without any fillers, is more resistant to water absorption compared to the filled composites (Altun et al., 2023). The composites containing CEL, WS, and WF exhibit progressively higher mass changes, but different trends occur for different filler contents.

Notably, the influence of filler content on water absorption is evident. In Figure 5a, where the composites contain 7.5 wt.% filler content, the water absorption increases in the following order: (the lowest) PHBV < WF7.5 < WS7.5, CEL7.5 (the highest) – the mass gain ranged from approx. 0.65% to 0.85%. Among them, CEL7.5 and WS7.5 showed slightly higher values compared to WF7.5. The most significant increase occurred during the initial stage of degradation (up to ~10 days), followed by a plateau, suggesting saturation of water uptake. A different trend was observed in Figure 5b, where the 15 wt.% filler composites exhibit a more pronounced increase in water uptake, with WF15 again demonstrating the highest mass change, followed by WS15,

CEL15, and PHBV. The mass change increased substantially, reaching about 1.1% for CEL15, 1.4% for WS15, and nearly 2.0% for WF15.

This behaviour can be attributed to the hydrophilic nature of the fillers. WS, CEL, and WF all contain polar hydroxyl groups that can readily interact with water molecules, leading to increased water absorption in the composite materials. The higher the filler content, the greater the potential for these interactions, as reflected in the more significant mass changes observed for the composites with 15 wt.% filler content compared to those with 7.5 wt.%.

The results suggest that increasing the filler content significantly enhances the hydrophilic properties of PHBV-based composites, which could be a crucial factor when considering the material's application in the environments where moisture absorption is a concern. This indicates that the surface chemistry and structure of the filler material strongly influence the overall behaviour of the composite during hydrolytic degradation.

In conclusion, the data from Figures 5a and 5b highlight the impact of filler content and type on the water absorption behaviour of PHBV-based composites. This behaviour should be carefully considered in the design of biodegradable composites for specific applications, particularly where moisture resistance is critical.

After 30 days of hydrolytic degradation in an aqueous environment containing a septic tank microbial preparation at 40 °C, significant changes were observed in the mechanical properties of PHBV-based composites with different natural fillers, and results were presented in Figures 6 and 7. The tensile strength of neat PHBV decreased by 10.8% (from 34.1 to 30.4 MPa), indicating

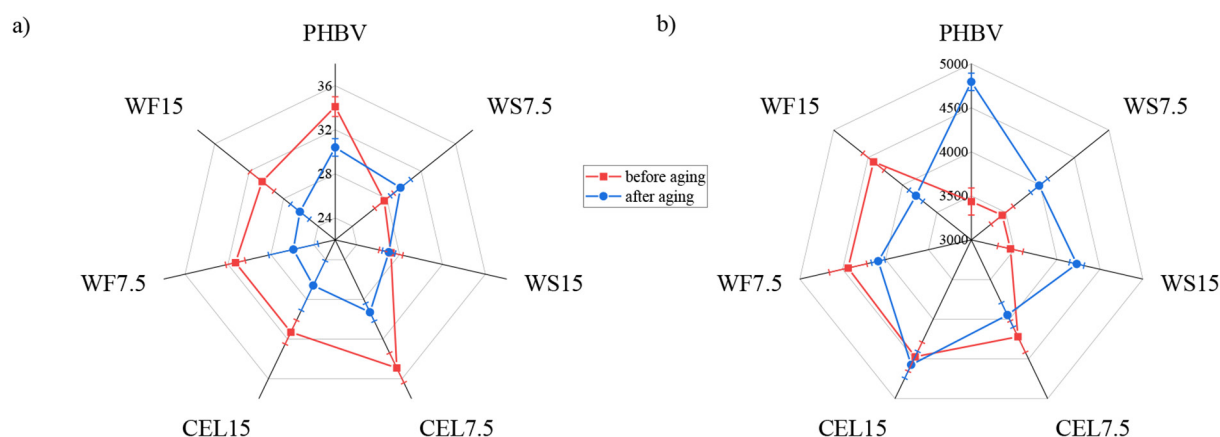


Figure 6. Mechanical properties of composites before and after aging: a) tensile strength and b) Young's modulus

hydrolytic chain scission and partial loss of polymer integrity. Interestingly, the composites with WS showed increased or stable tensile strength after incubation: WS7.5 exhibited a 6.9% increase (27.7 to 29.6 MPa), while WS15 remained almost unchanged (27.2 to 27.0 MPa). In contrast, the composites with CEL and WF showed significant deterioration: CEL7.5 and CEL15 lost 16.0% and 15.0%, respectively, and WF7.5 and WF15 lost 17.2% and 14.4%, respectively. Neat PHBV exhibited a substantial increase in stiffness (+39.6%, from 3436 to 4794 MPa), likely due to secondary crystallisation during incubation. WS-based composites also demonstrated improved Young's modulus values: WS15 increased by 22.4%, suggesting effective structural reinforcement. However, WF-based composites experienced a decrease in Young's modulus, especially WF15 (−13.9%), indicating matrix deterioration and poor filler-matrix interfacial adhesion after degradation.

The observed changes are attributed to several concurrent degradation mechanisms. Hydrolysis of ester bonds in the PHBV matrix likely initiated predominantly in the amorphous regions, leading to molecular weight reduction and loss of ductility. Enzymatic degradation by microbial enzymes, such as esterases and lipases present in the septic preparation, further accelerated the scission of polymer chains. The swelling behaviour of hydrophilic fillers like CEL and WF induced internal stresses at the filler-matrix interface, leading to debonding, microvoid formation, and reduced mechanical integrity. In parallel, secondary crystallisation in PHBV-rich regions likely contributed to the observed increase in Young's modulus, albeit at the expense of matrix toughness. Although WS-filled composites absorbed more water than

neat PHBV, they retained tensile properties more effectively. Therefore, water uptake alone cannot be used as a predictor of mechanical degradation. The retention of properties appears to be related to filler morphology and stress-transfer mechanisms rather than moisture absorption itself. Conversely, CEL and WF, due to their high hydrophilicity and less favourable interfacial compatibility, promoted faster degradation and structural disintegration of the composite matrix. Overall, WS-filled composites demonstrated superior mechanical stability, confirming their potential as reinforcement agents in biodegradable PHBV composites subjected to moist, biologically active environments. The results showed significant differences in tensile strength and Young's modulus for most composites ($p < 0.05$). Post-hoc Tukey's HSD test revealed the following:

- PHBV exhibited a significant decrease in tensile strength after degradation (from 34.1 to 30.4 MPa, $p < 0.05$), indicating the impact of hydrolysis.
- WS7.5 showed a significant increase in tensile strength after degradation (from 27.7 to 29.6 MPa, $p < 0.05$), while WS15 remained statistically unchanged (from 27.2 to 27.0 MPa, $p > 0.05$).
- CEL7.5 and CEL15 showed significant decreases in tensile strength (from 34.9 to 26.6 MPa and from 31.3 to 25.9 MPa, respectively, $p < 0.05$).
- WF7.5 and WF15 also exhibited significant reductions in tensile strength (from 31.3 to 25.8 MPa and from 30.5 to 26.1 MPa, respectively, $p < 0.05$).

The results of the study, as shown in Figure 7, indicate that the hydrolytic degradation of PHBV-based composites incorporating WS, CEL, and

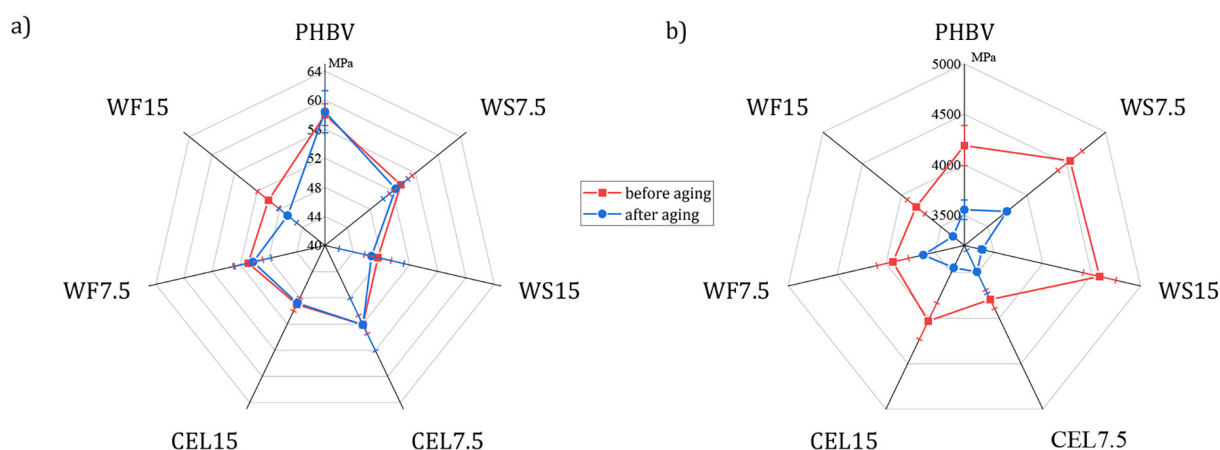


Figure 7. Mechanical properties of composites before and after aging: a) flexural strength and b) flexural modulus

WF caused only minor reductions in their flexural strength. Specifically, PHBV exhibited minimal change in its bending strength, from 58 MPa before degradation to 58.4 MPa after, suggesting that the material's mechanical properties remained largely stable. The composites containing CEL and WF showed slight decreases in flexural strength, with the WS composite experiencing a reduction from 53.4 MPa and 47.5 MPa to 52.5 MPa and 46.6 MPa.

Furthermore, the increase in standard deviation values observed in most composites post-degradation indicates a higher variability in the material's mechanical performance, possibly due to localised damage or microstructural changes caused by the hydrolytic process. This variability may result from uneven degradation across the composite structure, as the polymer matrix and filler materials degrade at different rates. The increase in standard deviations suggests that, while the overall mechanical performance remained relatively stable, the homogeneity of the materials was compromised.

When compared to the tensile test results, which were previously discussed, the flexural strength showed less pronounced degradation. In the tensile tests, a more significant drop in mechanical properties was observed, indicating that the materials may be more susceptible to tensile forces than bending stresses during the degradation process. This contrast highlights the need to consider different loading conditions when evaluating the durability of these composites, as bending and tensile behaviours may be influenced differently by the degradation mechanisms. The observed discrepancies between flexural and tensile properties further suggest that a more comprehensive understanding of the degradation

behaviour under various stress conditions is necessary for optimising the design of biodegradable composites for practical applications.

The statistical analysis showed that after hydrolytic degradation, the flexural strength of PHBV composites remained virtually unchanged ($p > 0.05$), with minimal changes in value. However, significant changes in flexural modulus were observed, particularly in WF composites ($p < 0.05$), where a notable decrease in stiffness occurred.

CONCLUSIONS

The study aimed to investigate the properties of PHBV composites containing natural waste-derived fillers, namely WS, CEL, and WF. Key findings include:

- In tensile properties, neat PHBV had a tensile strength of 34.1 MPa and Young's modulus of 3436 MPa. PHBV composites with 7.5 wt.% WF showed a tensile strength of 31.3 MPa and Young's modulus of 4437 MPa, while 15 wt.% WF exhibited a tensile strength of 30.5 MPa and Young's modulus of 4422 MPa. CEL composites, particularly PHBV/CEL15, showed a Young's modulus of 4472 MPa, but tensile strength decreased. WS composites had lower tensile strength, with PHBV/WS7.5 at 27.7 MPa and PHBV/WS15 at 27.2 MPa.
- In flexural properties, neat PHBV had a flexural strength of 58.0 MPa and a flexural modulus of 4190 MPa. PHBV/WF7.5 had a flexural strength of 50.9 MPa and a modulus of 3931 MPa, while PHBV/WF15 showed 47.5 MPa and 3814 MPa. WS composites showed modest changes, with

PHBV/WS7.5 at 53.4 MPa and PHBV/WS15 at 47.5 MPa. CEL composites increased flexural modulus from 3793 MPa (PHBV/CEL7.5) to 4032 MPa (PHBV/CEL15).

- Impact strength results showed neat PHBV at 12.0 kJ/m². Walnut shell composites (PHBV/WS7.5 and PHBV/WS15) reduced impact strength to 8.6 and 7.7 kJ/m², respectively. WF composites (WF7.5 and WF15) showed similar reductions. CEL composites improved impact strength, with CEL15 at 9.1 kJ/m² compared to CEL7.5 at 8.5 kJ/m².
- During hydrolytic degradation at 40 °C over 30 days, neat PHBV exhibited a low mass increase of approximately 0.3%. The incorporation of fillers significantly enhanced water uptake, reaching about 0.8% for PHBV/WS7.5 and up to ~1.4% for PHBV/WS15. The highest mass change was observed for PHBV/WF15 (~2.0%), indicating increased hydrophilicity with higher filler content.

Overall, the results indicate that walnut shell may contribute to maintaining selected mechanical properties after degradation, while cellulose and wood filler are more effective in enhancing stiffness. However, none of the fillers provided simultaneous improvement in all mechanical properties, highlighting the trade-offs associated with the incorporation of natural fillers into PHBV.

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REFERENCES

1. Antony Jose, S., Cowan, N., Davidson, M., Godina, G., Smith, I., Xin, J., Menezes, P. L. (2025). A comprehensive review on cellulose nanofibers, nanomaterials, and composites: Manufacturing, properties, and applications. *Nanomaterials* 2025; 15(356), <https://doi.org/10.3390/NANO15050356>
2. Bledzki, A. K., Jaskiewicz, A. Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibres - A comparative study to PP. *Composites Science and Technology*, 2010; 70(12), 1687–1696. <https://doi.org/10.1016/j.compscitech.2010.06.005>
3. Chan, C. M., Vandi, L. J., Pratt, S., Halley, P., Richardson, D., Werker, A., Laycock, B. Mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/wood flour composites: Effect of interface modifiers. *Journal of Applied Polymer Science*, 2018; 135(43). <https://doi.org/10.1002/APP.46828>
4. Conceição, M. N., dos Santos, M. C. C., Mancipe, J. M. A., Pereira, P. S. C., Ribeiro, R. C. C., Thiré, R. M. S. M., Bastos, D. C. A biodegradable composite of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with short cellulose fiber for packaging. *Materials Research*, 2023; 26(suppl 1), e20220615. <https://doi.org/10.1590/1980-5373-MR-2022-0615>
5. El-Taweel, S. H., Al-Hamdi, A. Starch as a successful biodegradable nucleating agent in biodegradable PHBV/PHO blends. *Journal of Thermal Analysis and Calorimetry*, 2024; 149(4), 1351–1364. <https://doi.org/10.1007/S10973-023-12791-0/FIGURES/4>
6. ISO 178:2019 - Plastics — Determination of flexural properties. (n.d.). Retrieved November 3, 2025, from <https://www.iso.org/standard/70513.html>
7. ISO 179-1:2010 - Plastics — Determination of Charpy impact properties — Part 1: Non-instrumented impact test. (n.d.). Retrieved November 3, 2025, from <https://www.iso.org/standard/44852.html>
8. ISO 527-1:2019 - Plastics — Determination of tensile properties — Part 1: General principles. (n.d.). Retrieved November 3, 2025, from <https://www.iso.org/standard/527-1>
9. Iso, B. S. E. N. Plastics — Determination of water absorption. In *Management*. 2008.
10. Jiang, H., Cheng, F., Hu, Y., Ji, Y., Hu, X., Ren, Y. Micro-mechanics modeling of compressive strength and elastic modulus enhancements in unidirectional CFRP with aramid pulp micro/nanofiber interlays. *Composites Science and Technology*, 2021; 206, 108664. <https://doi.org/10.1016/J.COMPSCITECH.2021.108664>
11. Jogur, G., Nawaz Khan, A., Das, A., Mahajan, P., Alagirusamy, R. Impact properties of thermoplastic composites. *Textile Progress*, 2018; 50(3), 109–183. <https://doi.org/10.1080/00405167.2018.1563369>
12. Jost, V., Langowski, H. C. Effect of different plasticisers on the mechanical and barrier properties of extruded cast PHBV films. *European Polymer Journal*, 2015; 68, 302–312. <https://doi.org/10.1016/J.EURPOLYMJ.2015.04.012>
13. Karmarkar, A., Chauhan, S. S., Modak, J. M., Chanda, M. Mechanical properties of wood-fiber reinforced polypropylene composites: Effect of a novel compatibilizer with isocyanate functional group. *Composites Part A: Applied Science and Manufacturing*, 2007; 38(2), 227–233. <https://doi.org/10.1016/j.compositesa.2006.05.005>
14. Khoshkava, V., Kamal, M. R. Effect of drying conditions on cellulose nanocrystal (CNC) agglomerate

- porosity and dispersibility in polymer nanocomposites. *Powder Technology*, 2014; 261, 288–298. <https://doi.org/10.1016/J.POWTEC.2014.04.016>
15. Kuciel, S., Liber-Kneć, A. Biocomposites based on PHB filled with wood or kenaf fibers. *Polimery/Polymers*, 2011; 56(3), 218–223.
16. Kuciel, S., Mazur, K., Jakubowska, P. Novel bio-renewable composites based on poly (3-hydroxybutyrate-co-3-hydroxyvalerate) with natural fillers. *Journal of Polymers and the Environment*. 2019. <https://doi.org/10.1007/s10924-019-01392-4>
17. Li, L., Liu, S., Du, G., Jiang, S., Yang, J., Zhang, J., Li, T. Sustainable engineering polymer composites fabricated using delignified bamboo fiber as reinforcement and walnut shell powder as filler. *Composites Part B: Engineering*, 2024; 287, 111857. <https://doi.org/10.1016/J.COMPOSITESB.2024.111857>
18. Mandala, R., Hegde, G., Kodali, D., Kode, V. R. From waste to strength: Unveiling the mechanical properties of peanut-shell-based polymer composites. *Journal of Composites Science* 2023; 7(8), 307. <https://doi.org/10.3390/JCS7080307>
19. Masłowski, M., Miedzianowska, J., Strzelec, K. The potential application of cereal straw as a bio-filler for elastomer composites. *Polymer Bulletin*, 2020; 77(4), 2021–2038. <https://doi.org/10.1007/S00289-019-02848-2/FIGURES/9>
20. McNeill, D. C., Pal, A. K., Nath, D., Rodriguez-Uribe, A., Mohanty, A. K., Pilla, S., Gregori, S., Dick, P., Misra, M. Upcycling of ligno-cellulosic nutshells waste biomass in biodegradable plastic-based biocomposites uses - a comprehensive review. *Composites Part C: Open Access*, 2024; 14, 100478. <https://doi.org/10.1016/J.JCOMC.2024.100478>
21. Meereboer, K. W., Meereboer, K. W., Pal, A. K., Misra, M., Misra, M., Mohanty, A. K., Mohanty, A. K. Sustainable PHBV/cellulose acetate blends: Effect of a chain extender and a plasticizer. *ACS Omega*, 2020; 5(24), 14221–14231. https://doi.org/10.1021/ACSOMEGA.9B03369/ASSET/IMAGES/MEDIUM/AO9B03369_M001.GIF
22. Mehdikhani, M., Gorbatiikh, L., Verpoest, I., Lomov, S. V. Voids in fiber-reinforced polymer composites: A review on their formation, characteristics, and effects on mechanical performance. *Journal of Composite Materials*, 2019; 53(12), 1579–1669. https://doi.org/10.1177/0021998318772152/ASSET/07D4A013-567C-47C0-AC2E-7BB97D3549E5/ASSETS/IMAGES/LARGE/10.1177_0021998318772152-FIG27.JPG
23. Naghmouchi, I., Espinach, F. X., Mutjé, P., Boufi, S. Polypropylene composites based on lignocellulosic fillers: How the filler morphology affects the composite properties. *Materials & Design* (1980–2015), 2015; 65, 454–461. <https://doi.org/10.1016/J.MATDES.2014.09.047>
24. Nishino, T., Matsuda, I., Hirao, K. All-cellulose composite. *Macromolecules*, 2004; 37(20), 7683–7687. <https://doi.org/10.1021/ma049300h>
25. Norouzpour, H., Hooman Hemmasi, A., Talaeipour, M., Bazyar, B., Abdouss, M., Hooman Hemmasi, A. Comparison of resistance and biodegradability properties of wood-plastic composites from wood flour/PHB/HDPE/STARCH. *Wood and Fiber Science*, 2022; 54(2), 81–89. <https://doi.org/10.22382/wfs-2022-09>
26. Pandey, J. K., Nakagaito, A. N., Takagi, H. Fabrication and applications of cellulose nanoparticle-based polymer composites. *Polymer Engineering & Science*, 2013; 53(1), 1–8. <https://doi.org/10.1002/PEN.23242>
27. Pradhan, P., Satapathy, A. Physico-mechanical characterization and thermal property evaluation of polyester composites filled with walnut shell powder. *Polymers and Polymer Composites*, 2022; 30. https://doi.org/10.1177/09673911221077808/ASSET/1E8529DB-52A7-4D8F-9811-BC02F85BD1AC/ASSETS/IMAGES/LARGE/10.1177_09673911221077808-FIG7.JPG
28. Qaiss, A., Bouhfi, R., Essabir, H., Qaiss, A., Bouhfi, R., Essabir, H. Effect of processing conditions on the mechanical and morphological properties of composites reinforced by natural fibres. *Manufacturing of Natural Fibre Reinforced Polymer Composites*, 2015; 177–197. https://doi.org/10.1007/978-3-319-07944-8_9
29. Sanchez-Safont, E. L., Cabedo, L., Gamez-Perez, J. Cellulose-reinforced biocomposites based on PHB and PHBV for food packaging applications. *Sustainable Food Packaging Technology*, 2021; 225–261. <https://doi.org/10.1002/9783527820078.CH8>
30. Schirp, A., Stender, J. Properties of extruded wood-plastic composites based on refiner wood fibres (TMP fibres) and hemp fibres. *European Journal of Wood and Wood Products*, 2010; 68(2), 219–231. <https://doi.org/10.1007/S00107-009-0372-7/FIGURES/15>
31. Venkatarajan, S., Subbu, C., Athijayamani, A., Muthuraja, R. Mechanical properties of natural cellulose fibers reinforced polymer composites – 2015–2020: A review. *Materials Today: Proceedings*, 2021; 47, 1017–1024. <https://doi.org/10.1016/J.MATPR.2021.05.547>
32. Xie, S., Xiao, F., Ma, S., Huo, S., Zhu, L., Song, H. Effect of colorants on interfacial compatibility in wood flour/poly (β-hydroxybutyrate valerate) composites. *Wood Material Science & Engineering*, 2025; 20(1), 150–158. <https://doi.org/10.1080/17480272.2024.2332793>
33. Zhang, D., He, M., Qin, S., Yu, J. Effect of fiber length and dispersion on properties of long glass fiber reinforced thermoplastic composites based on poly(butylene terephthalate). *RSC Advances*, 2017; 7(25), 15439–15454. <https://doi.org/10.1039/C7RA00686A>