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# Structure-property correlations study in biochar-enhanced polyamide composites for sustainable materials development

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# ABSTRACT

This study explores the synthesis and characterization of polyamide/biochar composites *via in situ* polymerization of 12-aminolauric acid with varying biochar concentrations. The motivation behind this research is to enhance the properties of polyamide 12 (PA12) by integrating biochar, a sustainable material derived from biomass, to improve both performance and environmental impact. A detailed structure-property correlation analysis was conducted to assess the effects of biochar on PA12's morphology, mechanical behavior, crystallinity, thermal stability, viscoelastic performance, and environmental sustainability. Key findings include successful PA12 synthesis, confirmed by FTIR and <sup>1</sup>H NMR spectroscopy. Increased biochar content led to a decrease in molecular weight and an increase in crystallinity from 27 % to 38 %, suggesting enhanced nucleation effects. SEM analysis showed excellent dispersion and compatibility of biochar within the PA12 matrix, leading to significant improvements in tensile strength (from  $38 \pm 1$  MPa to  $54 \pm 2$  MPa) and modulus (from  $745 \pm 30$  MPa to  $2055 \pm 65$  MPa). Rheological tests demonstrated shear-thinning behavior, facilitating effective extrusion-based 3D printing of a complex object with 50 wt% biochar. A life cycle assessment revealed substantial environmental benefits, including a net reduction of 1.83 kg-CO<sub>2</sub> equiv.·kg<sup>-1</sup> due to the use of biochar derived from wood pyrolysis. These findings highlight the potential of PA12/biochar composites as environmentally sustainable structural materials, combining enhanced functional properties with significant ecological advantages.

#### 1. Introduction

Plastics are prevalent in modern society, playing a crucial role in various industries and everyday life. However, the extensive use of conventional, fossil-based plastics has led to severe environmental consequences, including pollution and microplastics, habitat destruction, and harm to wildlife [1–3]. Blending bio-based particles with plastics presents a promising avenue to enhance the economic and environmental sustainability of plastic materials. By incorporating bio-based particles derived from renewable sources such as plant fibers or agricultural waste, reliance on finite fossil fuel resources can be reduced, and the environmental impact of plastic production can be mitigated [4–8]. For instance, the pyrolysis of agricultural waste, such as crop residues, straw, or husks, can yield biochar, a carbon-rich material.

Biochar obtained from agricultural waste can then be utilized as a filler or reinforcement in plastic formulations, improving mechanical properties and reducing the overall carbon footprint of the resulting plastic composites. This approach not only diverts agricultural waste from landfills but also contributes to the development of a more sustainable and circular economy [9–11].

Polyamides, PAs, commonly known as nylons, are a versatile class of synthetic polymers that exhibit a wide range of properties, including high strength, toughness, and chemical resistance, making them valuable materials in various industrial applications [12,13]. Due to the relatively high amount of amide groups in the backbone of traditional PAs like PA6 and the consequent higher hydrogen bonding density, they exhibit relatively high melting points, necessitating the use of significant energy during processing [14,15]. This energy-intensive processing

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contributes to environmental concerns, as it leads to increased energy consumption and greenhouse gas emissions. Additionally, traditional PAs are sensitive to water, which can adversely affect their mechanical properties and dimensional stability over time [16–18]. To address these challenges, the development of long-chain aliphatic polyamides with a lower number of amide groups in the polymer backbone has emerged as a viable solution. Polyamides such as PA11 and PA12 exhibit a lower number of amide groups compared to traditional PAs like PA6. As a result, they possess lower melting points and require less energy for processing, making them more environmentally friendly alternatives [13,19]. PA12, a long-chain aliphatic polyamide, is known for its excellent mechanical properties, low moisture absorption, and resistance to abrasion and chemicals. These qualities make PA12 a preferred choice for demanding applications such as automotive components, electrical insulation, and consumer goods [20,21].

However, PA12 is primarily derived from petroleum-based sources, contributing to environmental concerns associated with fossil fuel extraction and consumption. As the world seeks more sustainable alternatives to traditional plastics, there is a growing interest in reducing the environmental footprint of polymers like PA12. One promising solution to enhance the sustainability of PA12 is to compound it with biobased fillers with a low carbon footprint, such as biochar. Biochar serves as a renewable and abundant resource derived from organic waste streams that would otherwise be disposed of or incinerated, contributing to greenhouse gas emissions. By utilizing biochar as a filler, the mechanical properties and thermal stability of PA12 composites can enhanced. The porous structure of biochar provides increased surface area for interaction with the polymer matrix, leading to improved reinforcement and mechanical performance. Additionally, biochar's high thermal stability can enhance the heat resistance of PA12, expanding its potential applications in high-temperature environments [22,23]. Furthermore, by employing biochar, the environmental impact of PA12 production can be significantly reduced as it displaces a portion of petroleum-based raw materials. Nonetheless, a comprehensive life cycle assessment (LCA) is necessary to quantify and evaluate the overall environmental benefits and trade-offs associated with the incorporation of biochar in PA12 manufacturing processes.

A few studies have explored the environmental implications of incorporating biochar into polymer matrices. For instance, researchers have utilized cradle-to-gate life cycle assessment methodologies to investigate how the addition of biochar as a filler affects both material properties and environmental burdens. These studies have highlighted biochar's potential to reduce the environmental footprint of plastic materials, including recycled high-density polyethylene (PE), highdensity polyethylene (HDPE), polylactic acid (PLA), and polyhydroxybutyrate [24]. Furthermore, Tadele et al. [25] conducted a life cycle assessment of automotive applications, comparing the environmental impacts of Miscanthus biochar- and talc-reinforced polypropylene (PP) composites to assess their environmental performance. In addition, Roy et al. [26] evaluated the life cycle environmental impacts and benefits of automotive components manufactured from PP reinforced with biochar. Their findings indicated that replacing conventional components with innovative alternatives could aid in meeting fuel economy emission regulations in the automotive industry. However, despite these advancements, the literature notably lacks an LCA study regarding polyamide/biochar composites.

The incorporation of biochar into a PA12 matrix can be achieved through various methods, including melt compounding [27] and *in situ* polymerization [11]. In melt compounding, biochar particles are mixed with molten PA12 resin to form a homogeneous blend. This process typically involves extrusion or melt mixing equipment to ensure proper dispersion of biochar within the polymer matrix. While melt compounding is a widely used method for incorporating fillers into polymer matrices, it requires an additional processing step, which can be energy-consuming [28]. On the other hand, *in situ* polymerization involves the direct synthesis of PA12 in the presence of biochar particles.

During polymerization, biochar is dispersed within the polymer matrix as the polymer chains are formed around the filler particles. Unlike melt compounding, *in situ* polymerization does not require an extra processing step for incorporating biochar, making it a more streamlined process. Furthermore, *in situ* polymerization generally surpasses melt compounding in achieving uniform dispersion of fillers, such as biochar, within the polymer matrix. It also allows for the simultaneous formation of polymer chains and the incorporation of fillers, leading to better entanglement and interfacial adhesion between the polymer matrix and the filler particles. This simultaneous formation ensures that the fillers are uniformly dispersed and encapsulated within the polymer matrix during the polymerization process, resulting in enhanced dispersion compared to melt compounding, where fillers are added to an already-formed polymer matrix [11,29–31].

This study reports the synthesis of a range of polyamide/biochar composites via in situ polymerization of 12-aminolauric acid with varying concentrations of biochar for the first time. A comprehensive structure-property correlation analysis is conducted to assess the impact of biochar addition on various properties of the PA12 matrix, including morphological analysis, mechanical property evaluation, crystallinity behavior, thermal decomposition behavior, and viscoelastic performance. To showcase a practical application, the sample with the highest biochar concentration has been 3D printed into a complex object using material extrusion additive manufacturing. Additionally, for the first time, an LCA study is conducted to investigate the potential environmental benefits of integrating biochar into the PA12 matrix. Thanks to the biogenic CO<sub>2</sub> sequestration, together with the *in situ* polymerization requiring low energy consumption, notable benefits in terms of carbon footprint, cumulative energy demand, material resource scarcity, or acidification are obtained.

# 2. Experimental

#### 2.1. Materials

12-Aminolauric acid (purity >98.0 %), 1,1,1,3,3,3-hexafluoro-2propanol (HFIP), and trifluoroacetic acid potassium salt were procured from Tokyo Chemical Industry Co (TCI). Sodium hypophosphite monohydrate (purity ≥99 %), chloroform-d (99.8 atom %D), and trifluoroacetic anhydride (reagentPlus, purity ≥99 %) were sourced from Sigma Aldrich. Pine wood chips were supplied by a local vendor in Finland. They were subjected to heating at 550 °C with a heating rate of 5 °C/min and then maintained isothermally for 2 h. This carbonization process was conducted under a nitrogen atmosphere. The pyrolyzed sample was milled and sieved using a 70-µm mesh.

# 2.2. In situ polymerization and sample preparation

A stainless-steel reactor, equipped with an overhead mixer and a heating jacket, facilitated the polymerization process. The monomer, 12-aminolauric acid, was blended with a small quantity of sodium hypophosphite monohydrate catalyst (0.1 wt%) and heated to 240 °C under a vigorous nitrogen flow for 4 h. Following synthesis, the resultant polymer, PA12, was cooled under a nitrogen atmosphere to prevent oxidation and subsequently extracted from the reactor. The resulting polymer chunk underwent milling into smaller pieces using a Retsch SM 300 Cutting Mill device equipped with a 6 mm bottom sieve. In the case of biochar-containing composites, a predetermined quantity of biochar was initially mixed with the monomer. The subsequent polymerization steps mirrored those outlined for pure PA12. The quantity of side products, such as water vapor, was theoretically determined, assuming a 100 % yield for the polymerization process. A comprehensive structureproperty correlation study of biochar-enhanced polyamide composites was conducted. Three different biochar concentrations were selected: 10 wt%, 30 wt%, and 50 wt%, corresponding to low, medium, and high loadings, respectively. The composites were therefore designated as

PA12-BC10, PA12-BC30, and PA12-BC50. It should be noted that although increasing the biochar content beyond 50 wt% was considered feasible during polymerization, it was decided not to exceed this limit due to concerns that higher amounts might render the samples excessively brittle, as indicated by mechanical property considerations.

For tensile testing, dog-bone specimens measuring 3.2 mm  $\times$  2 mm  $\times$  2.2 mm (L  $\times$  W  $\times$  T) were fabricated using an injection molding device, specifically the Babyplast 6/12 from England. The digital photograph of the dog-bone sample prepared from the PA12-BC50 composite is depicted in Fig. S1. Additionally, for the rest of the characterizations, hop-pressed films were produced by melting and pressing the samples with a Fontijne TP 400. A force of 150 kN was applied during pressing, followed by cold pressing at approximately 15 °C to achieve uniform film formation.

# 2.3. Characterizations

# 2.3.1. Chemical structure study

The chemical structure of the synthesized PA12 was analyzed using Fourier transform infrared (FTIR) spectroscopy conducted on a PerkinElmer FTIR instrument equipped with an ATR device. The scans were performed in transmittance mode over a wavenumber range from 4000 cm<sup>-1</sup> to 500 cm<sup>-1</sup>, with a resolution of 4 cm<sup>-1</sup> and 16 scans. Prior to measurement, the device background was recorded using the same parameters. Additionally, the chemical structure of the synthesized PA12 was further examined using proton nuclear magnetic resonance (<sup>1</sup>H NMR) on a Bruker NMR Spectrometer model AV III 400, with 64 scans. Before measurement, PA12 was dissolved in a solvent mixture of chloroform-d and trifluoroacetic anhydride (90/10, V/V).

# 2.3.2. Size exclusion chromatography, SEC

The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and dispersity (D) were determined using the Agilent SEC system, comprising an Agilent 1100 HPLC G1311A quaternary pump, an Agilent 1100 ALS G1313A Autosampler, two Shodex HFIP-806 m columns with a HFIP-LG guard column, and an Agilent 1200 G1362 refractive index detector. The eluent employed was 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) containing 3 g/L potassium trifluoroacetate salt. Calibration of the instrument was performed using polymethyl methacrylate standards, with a flow rate set at 0.5 ml/min. Samples were dissolved at a concentration of 2 mg/mL. For composites, subsequent to dissolution, the mixture underwent filtration to eliminate biochar particles.

# 2.3.3. Scanning electron microscope, SEM

The microstructure of the biochar, pure PA12, and the synthesized biocomposites were examined using SEM images captured by the Zeiss Sigma VP device. Imaging was conducted under vacuum conditions with a voltage of 2 kV. Prior to imaging, all samples were coated with a thin layer of gold/palladium alloy (80/20) using the Sputter Coater ACE600 under vacuum. Imaging of the biochar was performed from its surface, while imaging of the pure PA12 and composite films was carried out from the cryofracture surface area.

# 2.3.4. Crystallinity study

The crystallinity of the sample was assessed using differential scanning calorimetry (DSC) conducted on a TA Instruments Discovery DSC model 250 Auto. Approximately 5 mg of the sample was sealed within a Tzero aluminum pan and subjected to cyclic heating and cooling. Specifically, under a nitrogen atmosphere, the sample was equilibrated at 0 °C and then heated to 200 °C at a rate of 10 °C/min. Subsequently, it was cooled back down to 0 °C at the same rate of 10 °C/min. The heating and cooling cycles were repeated twice, and data from the second cycle were utilized for the extraction of crystallization parameters, including melting temperature ( $T_m$ ), melting enthalpy ( $\Delta H_m$ ), crystallization temperature ( $T_c$ ), and crystallization enthalpy ( $\Delta H_c$ ). The sample's

crystallinity ( $\chi_c$ ) was calculated using Equation (1), where  $\Delta H_m^0$  represents the enthalpy of 100 % crystalline PA12 (209.3 J/g) [32], and  $x_b$  denotes the mass fraction of biochar in the composite.

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0 (1 - x_b)} \times 100 \tag{1}$$

The crystallinity of the sample was further analyzed through X-ray diffraction (XRD) using the PANalytical X'Pert model MPD Alpha 1 from the Netherlands. Signals were recorded in an angular range of  $5-40^{\circ}$  (20) under a voltage and current of 45 kV and 40 mA, respectively, utilizing X-ray radiation with a wavelength of 1.54 Å.

# 2.3.5. Mechanical properties

The mechanical properties of the samples were evaluated through tensile testing conducted on a Universal Tester Instron model 4204 following ASTM D638 Type V standards. Prior to testing, the samples were conditioned for 48 h at 23 °C and 55 % relative humidity. Subsequently, they were subjected to a 5 kN load cell and stretched at a constant rate of 5 mm/s. The resulting stress-strain curves were analyzed to determine key parameters, including tensile modulus (MPa), tensile strength (MPa), and elongation at break (%). At least five samples were subjected to tensile testing, and the mean value  $\pm$  standard deviation was reported and analyzed.

# 2.3.6. Thermogravimetric analysis

The thermal decomposition behavior of the sample was assessed by thermogravimetric analysis (TGA) using the TA Instruments TGA model 5500 to gain insight into its thermal stability. Approximately 10 mg of the sample was placed on a platinum pan and heated from 30 °C to 800 °C at a rate of 10 °C/min under a nitrogen atmosphere. The raw data were utilized to generate TGA and DTG thermograms (differential thermogravimetric analysis). Subsequently, the thermal decomposition parameters, including the temperature corresponding to 5 % weight loss (T<sub>5%</sub>), 10 % weight loss (T<sub>10 %</sub>), the temperature of maximum weight loss (T<sub>max</sub>), and the residue at 800 °C, were extracted, tabulated, and analyzed.

# 2.3.7. Characterization of viscoelastic properties

Dynamic mechanical analysis (DMA) was utilized to explore the viscoelastic behavior and mechanical properties of the sample across a temperature range from 0 °C to 200 °C. Strip-shaped sample, measuring 50 mm in length, 5.3 mm in width, and 0.5 mm in thickness, were prepared from the hop-pressed film. It was subjected to a multi-frequency-strain mode on a TA Instruments DMA model Q800, with pre-load, frequency, and strain set at 1 kN, 1 Hz, and 1 %, respectively. The resulting storage modulus (E'), loss modulus (E''), and loss factor (tan  $\delta$ ) were plotted against temperature for analysis.

Additionally, rheology measurements were conducted on an Anton Paar Physica rheometer model MCR 301 to further characterize the viscoelastic performance of the sample. The test was carried out at 230 °C to ensure full melting of the sample and relaxation of the polymer chains. A strain sweep test was initially performed at a fixed angular frequency of 10 rad/s, with shear strain increasing logarithmically from 0.01 to 100 %. This established the linear viscoelastic region for subsequent frequency sweep tests, where the angular frequency was increased logarithmically from 0.01 to 628 rad/s at a fixed shear rate of 1 %. The resulting trends of storage modulus (G'), loss modulus (G''), and complex viscosity ( $|\eta^*|$ ) versus angular frequency were plotted and analyzed.

# 2.4. Life cycle assessment

The *cradle-to-gate* environmental impacts of polyamide/biochar composites, synthesized *via in situ* polymerization, were comprehensively assessed using life cycle assessment (LCA) methodology in

accordance with ISO 14040/44 international standards [33–35]. For the sake of clarity, a summary of the methodology adopted for LCA is provided in Fig. S2. This assessment encompassed raw material acquisition, including upstream processes and transportation, energy requirements for on-site production, and waste management considerations. Notably, impacts associated with equipment use were excluded from the analysis. The total energy consumption was calculated by multiplying the maximum power of the equipment by its operational time, accounting for a 70 % utilization rate. To facilitate comparison and future research, the life cycle inventory (LCI) derived from the laboratory experiments is detailed in Tables S1–S4 and in the flowcharts provided in Figs. S3–S5.

Four distinct scenarios for biochar production were examined. Initially, the influence of electricity grid dynamics was explored, considering the energy intensity of the process. This involved evaluating a medium-voltage (1–24 kV) electricity mix representative of the average across 35 European countries (European Network of Transmission System Operators, ENTSO-E). Additionally, a scenario utilizing medium-voltage electricity sourced entirely from renewable sources (Swiss mix) was investigated. In both cases, the analysis accounted for electricity consumption, transmission infrastructure, and associated losses. Furthermore, the following modifications were made to assumptions concerning raw material procurement, waste treatment, and biogenic  $CO_2$  sequestration. These adjustments were implemented to refine the assessment and enhance its accuracy.

Wood chips are sourced either through direct purchase or obtained from waste streams, with the latter scenario necessitating transportation to the processing facility. Furthermore, the integration of a compact thermal oxidizer is proposed for the abatement of emitted CO, CH<sub>4</sub>, and hydrocarbons, ensuring clean combustion to produce solely CO<sub>2</sub> and H<sub>2</sub>O. This reaction typically occurs at temperatures ranging from 1000 to 1100 °C. In addition, in cases where wood chips are sourced from waste streams, a bio-waste treatment process can be modeled to account for the avoided environmental burden. Moreover, biogenic CO2 emissions are factored into the conversion process of wood chips to biochar. Emissions occurring during pyrolysis and subsequent combustion in the thermal oxidizer are balanced by the biomass's CO<sub>2</sub> absorption from the atmosphere. Consequently, the stable carbon sequestered within the biochar is recognized as the sole biogenic CO<sub>2</sub> contribution [36]. The life cycle impact assessment (LCIA) was performed using the OpenLCA 2.1.1 software coupled with the "ecoinvent v3.10 Cut-Off Unit Processes" database, available from January 2024. The details of the applied methodologies, as well as the functional units employed to standardize the impacts, are provided in the Supplementary Information (S1).

# 2.5. Additive manufacturing process

The milled sample was employed in printing an object utilizing a granular-based printer (Tumaker NX Pro Pellets) with a nozzle diameter of 0.8 mm. Printing parameters, including printing temperature, build-plate temperature, extrusion chamber temperature, and printing speed, were set to 230 °C, 100 °C, 170 °C, and 30 mm/s, respectively. The layer thickness was 0.2 mm, with 100 layers printed in total, resulting in an overall length of 19.9 mm for the object. Additionally, we experimented with different fan speeds and concluded that the best adhesion between the layers was achieved when the fan was turned off. The infill percentage was also set as 20 %. These parameters underwent experimental optimization to achieve the desired quality of the printed object. The CAD model was created using 3D Builder software. Moreover, dog bone samples were printed for subsequent mechanical testing. Both the digital photograph of the printed dog bone and the corresponding CAD model are provided in Fig. S6.

# 3. Results and discussion

# 3.1. Analysing chemical composition and molecular weight

The functional groups and chemical structure of the synthesized PA12 were examined using FTIR and <sup>1</sup>H NMR spectra, with the results depicted in Fig. 1. As illustrated in Fig. 1a, PA12 exhibited characteristic absorption bands typical of polyamides, such as hydrogen-bonded N-H stretching at 3285 cm<sup>-1</sup>, C-H vibrations of methylene groups - asymmetric and symmetric stretching at 2920 cm<sup>-1</sup> and 2852 cm<sup>-1</sup>, stretching of the amide groups at 1631  $\text{cm}^{-1}$  and 1549  $\text{cm}^{-1}$ , C-H bending at  $1462 \text{ cm}^{-1}$ , and strong C–N stretching of at  $1269 \text{ cm}^{-1}$  [37]. These absorption bands confirm the successful synthesis of PA12 via the employed polymerization process. The <sup>1</sup>H NMR spectrum of the synthesized PA12, illustrated in Fig. 1b, further confirmed the successful synthesis of polyamide, as the observed signals aligned with those reported for polyamides [6]. Specifically, signals detected at approximately 1.3 ppm and 1.6 ppm, designated as b and d, respectively, were attributed to proton signals originating from methylene groups from the aliphatic chains. The signal at around 2.7 ppm, labeled as a, was assigned to proton signals from methylene units adjacent to the carbonyl group, while those around 3.7 ppm, marked as c, were associated with proton signals from methylene units adjacent to the amino group. Signals from the solvents chloroform-d and trifluoroacetic anhydride are observed at 7.3 ppm and 10.4 ppm, respectively.

The molecular weight of a synthesized polymer plays a pivotal role in determining its mechanical properties and overall performance. Hence, we conducted measurements on different molecular weights of synthesized PA12, encompassing both the number average molecular weight (M<sub>n</sub>) and weight average molecular weight (M<sub>w</sub>), along with examining the polymer in the composites using SEC. Fig. 1c provides a visual representation of the SEC traces, while Table 1 summarizes the molecular weights and dispersity (Đ). Pure PA12 exhibited Mn and Mw values of 24400 g/mol and 62400 g/mol, respectively, aligning closely with literature values for polyamides [14,15,38]. Additionally, it displayed a relatively low dispersity of 2.5, indicating consistent molecular weights across the polymer chain population. This underscores enhanced material homogeneity and predictability in mechanical behavior [39]. This uniformity facilitates better control over crucial properties such as strength, stiffness, and ductility. Practically, polymers boasting a narrow dispersity index demonstrate enhanced processability during manufacturing and more reliable performance in end-use applications [40,41]. The observed moderate dispersity observed indicates a uniform chain length distribution, which is crucial for predictable mechanical properties. This uniformity can be attributed to the effective polymerization process, as suggested by the well-defined functional groups in the FTIR and <sup>1</sup>H NMR spectra. The consistent chemical structure ensures that the polymer chains grow at a similar rate, leading to a narrow molecular weight distribution.

Furthermore, the SEC traces exhibited a single distribution without any shoulders for pure PA12 and samples containing 10 and 30 wt% biochar. Nevertheless, in the case of the composite with 50 wt% biochar, a bimodal distribution is observed in the trace (Fig. 1c). In the composites, all molecular weights decreased with an increase in biochar content, indicating the interference of the biochar particles with the polymerization process, including the diffusion of monomers and byproducts. It's essential to note that despite the reduction in molecular weights observed in the composites, they still fall within the appropriate range reported for polyamides [15–17,32].

# 3.2. Structure-property correlation study

# 3.2.1. Microstructure analysis

The morphology of the prepared biochar, synthesized PA12, and composites were examined using SEM images. For the biochar, imaging was conducted from the surface of the particles, whereas for PA12 and



Fig. 1. a) FTIR spectrum, b) <sup>1</sup>H NMR spectrum, and c) GPC graph of the synthesized PA12.

Table 1Different molecular weights of the synthesized PA12 and composites.

Sample	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Đ
PA12	24400	62400	126000	2.5
PA12-BC10	20300	49000	86700	2.4
PA12-BC30	17000	45800	86800	2.7
PA12-BC50	12000	39600	94200	3.3

composites, it was performed on the cryo-fractured surface area. The resulting images are depicted in Fig. 2. The biochar particles (Fig. 2a) exhibited a diverse array of shapes and sizes, ranging from irregular fragments to spherical particles and agglomerates. Moreover, the surface of the biochar particles appeared rough or irregular, showcasing features such as cracks, crevices, and fissures. This surface irregularity was complemented by a porous structure, as evidenced in Fig. 2b, stemming from the decomposition of organic matter during pyrolysis [42,43]. These pores spanned from micropores to macropores, showcasing varied sizes and distributions, thereby offering an extensive surface area and an intricate network conducive to facilitating the diffusion of monomers and the growth of polymer chains within the biochar matrix. This porous architecture not only provided numerous active sites for monomer



Fig. 2. SEM images of a) and b) biochar, c) PA12, d) PA12-BC10, e) PA12-BC30, and f) PA12-BC50.

adsorption and polymerization but also promoted the thorough incorporation of polyamide within the biochar structure. Furthermore, the mechanical interlocking mechanism between the polymer chains and the irregular surface features of biochar enhanced the adhesion and stability of the polymer-biochar composite [9,44]. This synergy between the porous morphology of biochar and the polymerization process facilitated close contact and strong interfacial bonding between polyamide and biochar, potentially resulting in improved mechanical properties and enhanced thermal stability.

The SEM image of pure PA12, depicted in Fig. 2c, exhibited a notably smooth and continuous surface, characteristic of the polymer's resilience against fracture and deformation. The absence of prominent cracks or voids underscores the inherent toughness and cohesive nature of polyamide, showcasing its capacity to sustain structural integrity even under extreme conditions [45]. In contrast, the biochar-containing samples reveal a noticeably uniform dispersion of biochar particles within the polyamide matrix, indicating exceptional filler distribution throughout the composite material. This uniform dispersion suggests robust compatibility between the polyamide and biochar components, with effective intermixing observed at the microscopic level [11,46]. Specifically, Fig. 2d (PA12-BC10) shows a consistent distribution of biochar particles with no visible signs of clustering. The interface between the polyamide matrix and biochar appears well-integrated, suggesting strong interfacial bonding which is crucial for mechanical performance. Fig. 2e (PA12-BC30) continues to display uniform dispersion of biochar particles, though with a higher concentration compared to PA12-BC10. The increased biochar content did not compromise the adhesion between the polymer and biochar, as no cracks or voids were observed. This indicates that the processing technique maintains its effectiveness even with higher biochar loading. Finally, Fig. 2f (PA12-BC50) presents the highest concentration of biochar particles. Despite the substantial biochar content, the dispersion remains uniform, and the particles are well-integrated into the polymer matrix. The absence of agglomeration and the presence of strong interfacial bonding are still evident, highlighting the robustness of the processing method and the compatibility of the materials. Notably, the absence of particle agglomeration signifies the efficacy of the processing technique-specifically, in situ polymerization-employed during the synthesis of the polyamide/biochar composite. Overall, the SEM images showcase excellent dispersion, compatibility, adhesion, and the absence of crack formation or agglomeration, all of which contribute to the desirable properties and performance of the composite materials.

# 3.2.2. Crystallinity study

The crystallinity of both pure PA12 and the composites was investigated using DSC thermograms, as illustrated in Fig. 3a, with corresponding data summarized in Table 2. In pure PA12, a prominent endothermic peak at 178 °C, indicating its melting temperature, and a predominant exothermic peak at 151 °C, representing its crystallization temperature, were observed [47]. Additionally, a shoulder in the



Fig. 3. a) DSC thermograms and b) XRD patterns of pure PA12 and composites. c) Typical stress-strain curves. d) TGA and e) DTG thermograms of pure PA12, biochar, and composites. f) Storage modulus (E') and g) loss factor (tan  $\delta$ ) versus temperature. h) Complex viscosity and i) shear storage (G') and shear loss (G") moduli versus angular frequency at 230 °C and 0.1 % shear strain.

Table 2Crystallinity data extracted from DSC thermograms.

Sample	T <sub>m1</sub> (°C)	$T_{m2}$ (°C)	ΔH <sub>m</sub> (J/ g)	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/ g)	χ <sub>c</sub> (%)
PA12	172.8	178.6	56.5	151.5	48.5	27
PA12- BC10	171.9	178.6	55.1	148.7	50.6	29.2
PA12- BC30	173.7	179.1	45.6	150.5	36.3	31.1
PA12- BC50	171	177.7	39.8	151.4	40.1	38

melting peak at a lower temperature suggested the presence of either a separate crystalline structure or variations in crystal thickness [11]. In polyamides like PA12, two main crystal forms,  $\alpha$ - and  $\gamma$ -crystals, can typically occur.  $\alpha$ -phase crystals are the predominant and stable form, characterized by tightly packed molecular arrangements, resulting in higher density and more ordered structures. Conversely,  $\gamma$ -crystals are less common and less stable, often forming under specific conditions such as rapid cooling or specific processing methods. These crystals typically exhibit a less ordered molecular arrangement and lower density compared to  $\alpha$ -phase crystals [48,49]. To identify the crystal form, XRD analysis was conducted, as discussed below. Similar crystalline morphology was observed in the composites, indicating a likeness to that of pure PA12. Despite the addition of biochar, the melting and crystallization temperatures showed no significant changes; however, there was an increase in crystallinity. For instance, the crystallinity ( $\chi_c$ )

increased from 27 % in PA12 to 38 % in PA12-BC50. This increase suggests that biochar may function as a nucleating agent, fostering the formation of additional crystalline structures within the composite material [50]. In contrast to our findings, Alghyamah et al. [23] observed that the incorporation of biochar into a PP matrix resulted in an increased T<sub>m</sub> of the composites compared to neat PP. This increase was attributed to the heterogeneous nucleation effects induced by the rigid biochar fillers. Similarly, their study reported a relative increase in T<sub>c</sub>, suggesting that the biochar particles served as nucleation sites for crystal growth. Conversely, similar to our findings, Petousis et al. [51] found that the melting temperature of PP/biochar composites showed only minor variations regardless of the biochar loading. This lack of change in melting and crystallization temperatures in our study following the incorporation of biochar may be attributed to PA12 already possessing a well-established crystalline structure, where the presence of biochar particles did not disrupt or significantly alter the existing crystallization process.

XRD patterns were utilized to further investigate the crystalline structure of the synthesized PA12 and composites. The graphs are illustrated in Fig. 3b. All samples exhibited a predominant, sharp, and well-defined peak at approximately  $2\theta = 20^{\circ}$ , aligning with the main crystallographic plane or planes of the materials, namely  $\alpha$ -phase crystals [52,53]. The absence of any shoulder indicates a relatively homogeneous crystalline structure without significant variations or additional phases, corroborating the DSC findings of a single dominant crystalline structure observed in both pure PA12 and the composites. A broad peak observed at  $2\theta = 45^{\circ}$  suggests the existence of regions within the

synthesized polyamide where the polymer chains lack regular, crystalline arrangement, indicative of amorphous regions. Amorphous materials lack long-range order in their atomic or molecular arrangement, resulting in broad and diffuse peaks in XRD patterns. In contrast, biochar displayed a broad peak around  $2\theta = 23^{\circ}$ , indicative of an amorphous phase [54,55]. This peak was not discernible in the composites, likely due to its overlap with the dominant crystal peak of polyamide at  $2\theta = 20^{\circ}$ .

# 3.2.3. Mechanical properties assessment

The mechanical characteristics of composites hold significant importance in determining their practical utility. Hence, a comprehensive tensile testing regime was conducted to scrutinize the tensile mechanical attributes of both the synthesized PA12 and its composite counterparts. The representative stress-strain curves are presented in Fig. 3c, while Table 3 provides various mechanical parameters, encompassing tensile strength, tensile modulus, and tensile strain. PA12 exhibited a commendable tensile strain of 300  $\pm$  10 %, complemented by a tensile strength of  $38 \pm 1$  MPa and a tensile modulus of  $745 \pm 30$ MPa, in line with the literature values [56]. Upon the introduction of biochar, the tensile strength and modulus exhibited systematic increments, albeit at the cost of reduced tensile strain. For instance, upon incorporating 50 wt% biochar, the tensile strength, and modulus surged to 54  $\pm$  2 MPa and 2055  $\pm$  65 MPa, respectively, while the elongation at break diminished to 8  $\pm$  0.3 %. In other words, the composite became stronger and stiffer but less ductile.

These findings underscore the favorable compatibility between biochar and polyamide, along with the superior dispersion of biochar within the polyamide matrix, which collectively contributes to the improved tensile strength and modulus, albeit at the expense of reduced elongation at break. Such promising outcomes stem from the employed synthesis methodology, particularly the *in situ* polymerization technique. Through this method, biochar is efficiently dispersed and anchored within the polyamide matrix during the polymerization process, thereby ensuring robust interfacial adhesion between the two constituents. This enhanced compatibility facilitates the efficient transfer of mechanical loads across the composite, consequently enhancing its tensile strength and modulus. Moreover, the uniform dispersion of biochar particles serves to prevent the formation of stress concentration points within the matrix, thereby further bolstering the overall mechanical integrity of the composite material.

It is worth mentioning that the increased tensile strength and modulus with higher biochar content correlate with the enhanced crystallinity observed in DSC analysis, where crystallinity increased from 27 % in pure PA12 to 38 % in PA12-BC50. Greater crystallinity generally enhances material rigidity and load-bearing capacity. The GPC analysis also revealed a decrease in molecular weight with higher biochar content, which can impact toughness and elongation. However, the improved dispersion and interfacial bonding provided by biochar likely mitigated some of these negative effects, contributing to the observed increase in tensile strength and modulus.

Similar findings regarding biochar composites have been documented in the literature. For instance, in a study involving a PP matrix, the tensile strength and tensile modulus improved from 32.6 MPa to

1.53 GPa, respectively, to 33.1 MPa and 4.7 GPa with the addition of 24 % biochar [57]. Similarly, in the case of a PLA matrix, the tensile strength and tensile modulus increased from 37.3 MPa to 1.25 GPa to 74.53 MPa and 1.77 GPa, respectively, following the incorporation of approximately 8 wt% biochar [58,59]. Additionally, Anerao et al. [60] observed that adding 5 wt% biochar to the PLA matrix resulted in an ultimate tensile strength of 36 MPa and a modulus of elasticity of 1103 MPa. Moreover, it has been noted that a filler loading of 5 wt% enhanced the tensile strength of PLA by approximately 54 % while slightly increasing elongation, thus improving the toughness of the composites [61]. However, it is worth noting that in certain instances, a decline in the mechanical strength of the matrix has been reported due to the lack of compatibility between biochar particles and the matrix. Nevertheless, upon the introduction of a compatibilizer, significant improvements were observed. For example, Huang et al. [62] reported a decrease in the tensile strength of polybutylene succinate with the incorporation of 20 wt% biochar. However, the introduction of silane-modified biochar led to a substantial enhancement in tensile strength, elevating it from 33.40 MPa to 40.16 MPa.

Overall, it can be concluded that integrating biochar into polymer matrices leads to substantial enhancements in mechanical properties, notably in tensile strength and modulus, thereby yielding stiffer and more resilient materials. However, this integration also increases the brittleness of the polymer matrix, as evidenced by a reduction in elongation at break. This brittleness is expected due to biochar's inherent rigidity, which typically decreases the elongation of composite samples. In the current study, the lowest observed elongation was 8 % in the composite with the highest biochar loading of 50 wt% (PA12-BC50), which remains suitable for various applications. This biochar-enhanced composite holds potential for use in sectors requiring high strength and stiffness, such as automotive components.

To investigate the impact of 3D printing on the mechanical properties of the developed composites, dog bone specimens were printed using the PA12-BC50 sample and subjected to tensile testing under the same parameters used for the injected molded samples. The typical stress-strain curve is included in Fig. 3c, and the relevant data are summarized in Table 3. Compared to the injected molded sample, all the mechanical properties were reduced in the 3D-printed sample. For instance, the tensile strength dropped from  $54 \pm 2$  MPa to  $31 \pm 1$  MPa, and the tensile modulus decreased from  $2055 \pm 65$  MPa to  $1808 \pm 53$ MPa. These reductions could be due to the layer-by-layer nature of the 3D printing process, which often results in anisotropic properties and weaker interlayer bonding. Additionally, the presence of voids and imperfections inherent in the 3D printing process may also contribute to the observed decrease in mechanical performance [63,64].

# 3.2.4. Thermal stability investigation

The thermal stability of the synthesized PA12 and composites was examined by TGA to investigate the dispersion of biochar inside the polyamide matrix and the compatibility between phases. The TGA and DTG thermograms are plotted in Fig. 3d and e. Derived from the pyrolysis of organic biomass under controlled conditions, biochar is predominantly composed of highly aromatic carbonaceous structures with a low content of volatile matter. This chemical composition endows

Table 3

Different mechanical properties of pure PA12 and composite
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Sample	Tensile modulus (MPa)	Tensile strength (MPa)	Tensile strain (%)
PA12	$745\pm30$	$38 \pm 1$	$300\pm10$
PA12-BC10	$925\pm35$	$39\pm1.1$	$191\pm 6$
PA12-BC30	$1515\pm49$	$41 \pm 1.5$	$73\pm2$
PA12-BC50	$2055\pm65$	$54\pm2$	$8\pm0.5$
PA12-BC50 <sup>a</sup>	$1808 \pm 53$	$31\pm1$	$3\pm0.3$

<sup>a</sup> The 3D printed specimen.

biochar with exceptional resistance to thermal degradation, making it highly stable even at elevated temperatures. This stability was evident in the TGA curve presented in Fig. 3d, where biochar demonstrated minimal weight loss of approximately 10 % at a relatively high temperature of 800 °C. Such characteristics render biochar a valuable additive for enhancing the thermal properties of composite materials, contingent upon its uniform dispersion within the polymer matrix and appropriate compatibility with it. As depicted in Fig. 3d and summarized in Table 4, all decomposition temperatures significantly increased upon the addition of biochar. For instance,  $T_{5\%},\,T_{10}$  %, and  $T_{max}$  shifted from 416  $^\circ\text{C},$ 426 °C, and 456 °C in PA12, respectively, to 434 °C, 443 °C, and 467 °C in PA12-BC50. These shifts suggest robust interactions between biochar and polyamide, corroborating the excellent dispersion of biochar within the polyamide matrix and its compatibility with the polymer, facilitated by the employed in situ polymerization for composite fabrication. Furthermore, the char residue at 800 °C, reported in Table 4, was utilized to assess the dispersion of biochar within the polyamide matrix. The agreement between the experimental and theoretical char residues for the composites, relative to pure PA12 and biochar, underscores the uniform dispersion of biochar within the polyamide matrix.

Similar observations regarding the thermal stability of biochar-based composites have been documented in the literature. For example, Ahmetli et al. [65] demonstrated that plastic waste char and pine cone char could notably enhance the thermal stability of neat epoxy resin at temperatures exceeding 300  $^{\circ}$ C. Additionally, the T<sub>5%</sub> (temperature at 5 % weight loss) increased from 387.3 °C for pure PP to 442.1 °C with 10 wt% biochar [51]. Similarly, significant improvements in thermal performance were observed in PP filament composites loaded with 0.75 wt % ultrasonicated biochar, showing effective increases in onset temperature and maximum decomposition rate by 51 °C and 40 °C, respectively [66]. Moreover, Alghyamah et al. [23] concluded that the addition of biochar particles to PP matrices enhanced thermal stability by delaying the onset and maximum decomposition temperatures while yielding high biochar residues. Similarly, substantial enhancements in the thermal stability of PLA were reported following biochar incorporation [58, 67.68].

Several mechanisms contribute to enhancing the thermal stability of polymers, such as polyamides, upon biochar incorporation. Biochar particles act as physical barriers within the polyamide matrix, impeding heat diffusion and polymer chain degradation, thereby bolstering thermal stability. Additionally, biochar may foster the formation of stable carbonaceous char during thermal degradation. This char layer serves as a protective shield, mitigating further degradation by insulating the polymer matrix from heat and oxygen [69]. Furthermore, the high heat capacity of biochar particles enables significant heat energy absorption during thermal decomposition, diminishing temperature gradients within the composite material and attenuating thermal degradation of the polyamide matrix.

Notably, this enhanced thermal stability can be linked to the mechanical properties observed in the tensile testing results. The increased tensile strength and modulus of the composites are consistent with improved thermal properties, as the uniform dispersion of biochar within the polyamide matrix, as confirmed by TGA, likely contributes to better load distribution and reduced stress concentration, which aligns

 Table 4

 Thermal decomposition data extracted from TGA and DTG curves.

	-			
Sample	T <sub>5%</sub> (°C)	T <sub>10 %</sub> (°C)	$T_{max}$ (°C)	Residue material at 800 °C (%)
PA12	416	426	456	0
PA12-	424	436	466	10
BC10				
PA12-	430	438	466	22
BC30				
PA12-	434	443	467	44
BC50				
Biochar	540	763	-	89

with the enhanced mechanical performance. The increased crystallinity observed in the DSC analysis (from 27 % in pure PA12 to 38 % in PA12-BC50) supports this, as higher crystallinity typically correlates with increased rigidity and thermal stability.

# 3.2.5. Study of viscoelastic properties

DMA was utilized to explore the viscoelastic properties of the synthesized PA12 and composites across varying temperatures, aiming to explore the dispersion of biochar within the polyamide matrix and its interaction with the polymer. Fig. 3f and g depict the behavior of the storage modulus (E') and the loss factor (tan  $\delta$ ) in relation to temperature. In pure PA12, E' remained relatively constant at low temperatures, indicative of a glassy or highly ordered state characterized by immobilized polymer chains and a rigid structure. However, as temperature increased, E' declined, signifying enhanced polymer chain mobility and relaxation, which are often associated with the glass transition temperature (Tg). Near and above Tg, E' reduction occurred due to increased polymer chain movement, transitioning from a glassy to a rubbery state, resulting in decreased stiffness and increased flexibility [70,71]. Similar trends were observed in composites; however, E' exhibited a significant increase with the addition of biochar. For instance, at 30 °C, E' increased from 1270 MPa in PA12 to 3400 in PA12-BC50, marking approximately a 170 % improvement, indicating heightened stiffness. This enhancement underscores the homogeneous dispersion of biochar within the polyamide matrix and the strong interactions between biochar and the polymer [9,72]. Tan  $\delta$ , representing the damping behavior, is defined as the ratio of the loss modulus (E") to the storage modulus (E'). The peak of the tan  $\delta$  curve indicates the temperature at which the most significant transition from a glassy to a rubbery state occurs, denoting the  $T_g$ .  $T_g$ , determined from DMA, was approximately 65 °C for PA12, consistent with the literature [73]. Upon the addition of biochar, Tg slightly increased, suggesting improved compatibility between biochar and the polyamide matrix, potentially reinforcing it and affecting polymer chain mobility near the glass transition region [74,75]. This notion is further supported by the investigation of the tan  $\delta$  peak height, which reflects polymer chain mobility. The systematic reduction in peak height with the addition of biochar suggests decreased molecular mobility where polymer chains are more constrained and exhibit reduced movement during the transition [76].

Rheological measurements were employed to examine the uniform dispersion of biochar within a polyamide matrix and to evaluate the interaction between phases by analyzing the viscoelastic properties. To identify the linear viscoelastic region, a strain sweep test was initially conducted, where the shear strain was logarithmically increased from 0.01 % to 100 % at a constant angular frequency of 10 rad/s. At low strain rates, storage modulus (G') and loss modulus (G'') remained relatively constant and independent of strain amplitude (Fig. S3). This indicates the material's linear viscoelastic behavior, governed primarily by elasticity and adhering to Hooke's law. Subsequently, a shear strain of 1 % was selected for the subsequent frequency sweep test to ensure operation within the linear viscoelastic region.

The frequency sweep test was conducted at a fixed shear strain rate of 1 %, with the angular frequency ranging logarithmically from 0.01 rad/s to 628 rad/s. The results illustrating the behavior of complex viscosity, G', and G" versus frequency are plotted in Fig. 3h and i. Both pure PA12 and composites exhibited Newtonian behavior at low frequencies, with the complex viscosity remaining relatively constant, indicating viscous flow dominance over elastic character. However, at higher frequencies, the viscosity decreased, indicating shear thinning nature attributed to the disruption of polymer chain entanglements and physical bonding within the material. Furthermore, the interfacial bonding between the polyamide matrix and the reinforcement material may be compromised at higher frequencies, resulting in decreased viscosity [77,78]. While the same trend was observed for both PA12 and composites, the viscosity significantly increased with the addition of biochar particles. For example, the zero shear rate viscosity increased from  $2.7 \times 10^6$  mPa s in PA12 to  $3.7 \times 10^7$  mPa s in PA12-BC50, indicating a notable enhancement attributed to the confinement and immobilization of polymer chains around the filler particles, hindering polymer chain mobility and leading to a more viscous material. Moreover, biochar particles may contribute to the formation of physical entanglements and interactions within the polyamide matrix, further increasing viscosity [50,79,80]. This observed shear thinning behavior is advantageous in extrusion-based processes such as material extrusion 3D printing due to its impact on material flow and printability, as discussed in the following section [81].

The trend of G' and G" versus frequency provided insight into the impact of biochar addition on the viscoelastic properties of PA12. Both G' and G" increased with increasing frequency values. At higher frequencies, the time available for molecular relaxation decreases, resulting in an apparent increase in stiffness (G') and viscosity (G") of the material. In all samples, except for PA12-BC50, G<sup>"</sup> exceeded G<sup>'</sup> across the frequency range, indicating predominantly liquid-like behavior, with energy dissipation surpassing energy storage [82]. Conversely, in PA12-BC50, where G' exceeded G'', a more solid-like character was indicated, suggesting increased resistance to deformation and a higher ability to store energy rather than dissipate it [83]. Furthermore, both G' and G<sup>"</sup> increased systematically with the addition of biochar, indicating a reinforcement effect and suggesting that biochar particles contribute to the overall stiffness of the composite material through enhanced filler-matrix interactions and altered microstructural characteristics [84, 85]. The observed improvement in the viscosity of polyamide, as well as the storage and loss moduli upon the addition of biochar, strongly supports the uniform dispersion of the reinforcing filler within the polyamide matrix and underscores the outstanding compatibility between phases.

Thus, the combined insights from viscoelastic properties, mechanical properties, and TGA results highlight the enhanced performance of the biochar-reinforced composites. These findings illustrate that the uniform dispersion of biochar particles within the PA matrix, coupled with effective interactions facilitated by physical entanglements and strong interfacial bonding, significantly reinforces the polyamide matrix. This improvement is attributed to the *in situ* polymerization method used in the composite fabrication.

#### 3.3. Environmental impacts

The materials developed in this study adhere to circularity principles and predominantly utilize renewable resources. However, it's crucial to recognize that bio-based materials, while aligned with sustainability goals, may not inherently exhibit low environmental impacts due to additional burdens incurred during processing. Therefore, a life cycle assessment (LCA) was employed to rigorously quantify these environmental impacts and assess the overall sustainability of the developed materials. In particular, the climate change potential indicator was scrutinized, given its pivotal role in global long-term climate strategies. The assessment focused on quantifying  $CO_2$  emissions equivalents, shedding light on the environmental implications of the materials' development process. Fig. 4 illustrates the disaggregated climate change potential attributed to biochar production from wood chips, showcasing the nuanced impact of different production scenarios. Four distinct scenarios were considered, each offering insights into the varying environmental footprints associated with different production methodologies.

- 1. Wood chips are acquired for biochar production, treating them as raw materials. The process operates using a fossil-based medium-voltage electricity mix. Scenario A Fossil-Based.
- 2. Wood chips are sourced from waste streams, with a thermal oxidizer employed to mitigate combustion gases. Carbon sequestration is factored into the model. The process utilizes a fossil-based mediumvoltage electricity mix. Scenario B – Fossil-Based.
- 3. Wood chips are procured for biochar production, treating them as raw materials. The process is powered by a fully renewable medium-voltage electricity mix. Scenario A 100 % Renewable.
- 4. Wood chips are obtained from waste streams, with a thermal oxidizer utilized to mitigate combustion gases. Carbon sequestration is incorporated into the model. The process operates using a fully renewable medium-voltage electricity mix. Scenario B 100 % Renewable.

As depicted by the star in Fig. 4 (further details in Table S5), the environmental impacts range from  $-1.83 \text{ kg} \cdot \text{CO}_2$  equiv.  $\text{kg}^{-1}$  to +3.62kg·CO<sub>2</sub> equiv.  $kg^{-1}$ . A negative value denotes net environmental benefits, indicating that the production of 1 kg of biochar can sequester 1.83 kg of CO<sub>2</sub> equivalent gases. This is primarily due to the 1.96 biogenic CO2 sequestered by wood chips per 1 kg of biochar produced. Additionally, the avoidance of incineration of wood waste yields a further benefit of 0.14 kg·CO<sub>2</sub> equiv.·kg<sup>-1</sup>. However, realizing net environmental benefits necessitates the utilization of a renewable electricity mix alongside biogenic CO<sub>2</sub> sequestration, as fossil-based electricity consumption results in emissions ranging from 3.41 to 4.33 kg·CO<sub>2</sub> equiv. kg<sup>-1</sup> in scenario A. Notably, the greenhouse gas emissions obtained remain notably lower compared to conventional carbonaceous materials of similar characteristics (environmental impacts for benchmark carbon materials provided in Table S6), such as charcoal (1.87 kg·CO<sub>2</sub> equiv.  $kg^{-1}$ ), carbon black (2.51  $kg \cdot CO_2$  equiv.  $kg^{-1}$ ), and activated carbon  $(3.42 \text{ kg} \cdot \text{CO}_2 \text{ equiv. kg}^{-1})$ . In comparison with literature findings on the long-term sequestration of stable carbon found in biochar, various values have been reported: 0.89 kg CO2 equiv. per kilo for pyrolyzed yard waste (also considering avoided compost) [36], -2.06 kg·CO<sub>2</sub> equiv. per kilo for willow biochar production [86], -0.70 to -1.30kg·CO2 equiv. per kilo of feedstock processed (based on the assessment of ten different feedstocks) [87], or -2.11 to -2.56 kg·CO<sub>2</sub> equiv. per



Fig. 4. Disaggregated climate change potential for 1 kg of biochar production under four scenarios. The five-pointed star indicates the total climate change for each case.

kilo of generated biochar [88].

To delve deeper into the environmental sustainability of the developed materials, the environmental impacts of PA12 and its biochar composite variants were quantified, with summarized findings presented in Fig. 5 (refer to Table S7 for comprehensive details). A value of -1.83 kg·CO<sub>2</sub> equiv. per kilogram of biochar was adopted for modeling the composite materials, drawing from literature data ranging between -2.56 and -0.89 kg·CO<sub>2</sub> equiv.·kg<sup>-1</sup>. This value incorporates considerations for the prospective transition toward a fully renewable electricity grid alongside the potential utilization of biochar in medium to long-term structural applications as a filler. The climate change potential of neat PA12, synthesized via in situ polymerization of 12-aminolauric acid, was determined to be 4.06 kg·CO<sub>2</sub> equiv.·kg<sup>-1</sup>. Integration of biochar into PA12 formulations yielded a progressive reduction in greenhouse gas emissions, reaching a minimum of 1.10 kg·CO<sub>2</sub> equiv.  $kg^{-1}$  for the PA12-BC50 formulation. These reduced values significantly undercut the carbon footprint of 100 % virgin benchmark polyamide materials sourced from fossil origins, such as nylon 6 (9.89 kg·CO<sub>2</sub> equiv.  $kg^{-1}$ ) and nylon 6-6 (8.65 kg·CO<sub>2</sub> equiv.  $kg^{-1}$ ), as observed in the utilized database (Table S6). The process developed here for PA-12 nanocomposites also produces similar environmental impacts in the majority of impact categories when compared to other material alternatives with potential environmental benefits, including cellulosic fibers, plywood, polyester-complexed starch biopolymer, or polylactide. This underscores the efficacy of 12-aminolauric acid in fabricating polyamides with markedly lower environmental footprints.

To provide a holistic view of the sustainability of the developed

materials, eight additional impact metrics were considered. According to data gleaned from the ReCiPe 2016 v1.03, Midpoint (H) analysis, PA12/biochar composites demonstrate comparable impacts to nylon 6 and nylon 6-6 in terrestrial acidification and particulate matter categories. These findings are particularly promising considering the pilotscale nature of the materials under examination, indicating potential for further optimization and impact mitigation. Conversely, notable disparities emerge in freshwater eutrophication, water use, and especially in land use, where significantly larger impacts are observed. These disparities predominantly stem from the substantial requirements for water, land, and fertilizers during the acquisition of 12-aminolauric acid, contributing 91.7 %, 75.5 %, and 96.9 %, respectively, to the total impact of neat PA12.

In addition to assessing direct emissions, it's imperative to evaluate resource-oriented indicators to comprehensively gauge the environmental sustainability of the developed materials. Thus, the impacts of these materials on mineral resources were scrutinized using the crustal scarcity indicator (CSI). Measured in kilograms of silicon equivalents, this impact category holds relevance in the contemporary landscape of critical raw material scarcity, offering insights into potential long-term global elemental shortage issues. Notably, the material resources category (metals/minerals) showcases distinct advantages over nylon 6 and nylon 6-6 as the concentration of biochar increases within the composites, resulting in reduced CSI values. Consequently, the developed composites demonstrate the potential to mitigate the depletion of Earth's crustal elements compared to benchmark polyamides. Furthermore, the Cumulative Energy Demand (CED) was obtained as another



Fig. 5. Cradle-to-gate environmental impacts for PA12/biochar composites based on 1 kg of material. For comparison, the impacts originating from nylon and other material alternatives sharing potential environmental sustainability benefits are shown according to the ecoinvent v3.10 database.

pertinent resource-oriented indicator. It encompasses both direct and indirect energy usage, encompassing energy requirements for raw material extraction, processing, and disposal stages of raw and auxiliary materials [89]. In terms of non-renewable CED, the bio-based PA12 presents clear advantages, reflecting a low fossil-energy intensity process with values ranging from 18.2 to 35.0 MJ-equiv. This is notably lower than the 125.9 and 140.3 MJ-equiv. recorded for nylon 6 and nylon 6-6, respectively. However, it's crucial to acknowledge that the high bio-based content of PA12 is reflected in its larger renewable CED values.

# 3.4. Additive manufacturing

Additive manufacturing (AM) enables the layer-by-layer fabrication of intricate three-dimensional (3D) objects directly from digital designs, offering unique design flexibility, rapid prototyping capabilities, and customization possibilities [90,91]. Particularly in polymer and composite materials, AM has experienced exponential growth in demand and adoption in recent years, fundamentally transforming traditional manufacturing processes [92,93]. By facilitating the production of lightweight, durable, and intricately designed components with enhanced mechanical properties and performance characteristics, AM has revolutionized the industrial landscape [94,95]. However, the design of suitable materials for AM presents its own set of challenges. For instance, in extrusion-based techniques, materials must exhibit specific rheological properties to ensure optimal flow through the printer nozzle and adherence to previous layers. They must demonstrate appropriate viscosity, shear-thinning behavior, and thermal stability to promote uniform deposition and minimize printing defects such as nozzle clogging, stringing, or warping. Additionally, the materials should provide excellent interlayer adhesion and mechanical strength to guarantee the structural integrity and reliability of printed parts [96, 97].

PA12 is widely used in additive manufacturing, particularly in material extrusion (ME), due to its excellent mechanical properties, chemical resistance, and stability [98,99]. However, traditional PA12 is derived from non-renewable petroleum sources and has a significant environmental footprint. This study demonstrated that the integration of biochar into PA12 presented a sustainable alternative with several advantages. For instance, biochar could improve the tensile strength, stiffness, and impact resistance of PA12, making the resulting composites more robust and suitable for demanding applications. Moreover, biochar could enhance the thermal decomposition behavior of PA12, making it more suitable for high-temperature applications and increasing its lifespan. Furthermore, the LCA study proved that the incorporation of biochar, which sequesters biogenic CO<sub>2</sub>, helped in reducing the overall carbon footprint of the material. Utilizing biochar, a low-cost filler, may also reduce the overall material costs, making the composite more economically viable for large-scale manufacturing. Consequently, the printability of the developed composites as a greener and more sustainable alternative to commercial PA12 was investigated in this study. Subsequently, a PA12-BC50 sample was utilized to print a mesh object using a 3D Pellets Printer. Initially, challenges with poor flowability of the composite, delamination of the first printed layers from the belt, and issues with layer adhesion were encountered. Optimal settings were identified through systematic adjustments of various printing parameters. After numerous trials, the optimal parameters were determined to be a printing temperature of 230 °C, a build-plate temperature of 100 °C, an extrusion chamber temperature of 170 °C, and a printing speed of 30 mm/s.

Consequently, the molten PA12-BC50 displayed excellent flowability under printing conditions, facilitating precise material deposition and yielding a high-quality printed mesh object with intricate details and uniform layers, as depicted in Fig. 6. The molten samples flowed smoothly from the nozzle, depositing evenly and precisely. As a result, 100 layers were printed smoothly without encountering common issues in extrusion 3D printing, such as nozzle clogging, delamination, misalignment, or warping. Notably, despite the high biochar content (up to 50 wt%), all formulations demonstrated shear-thinning behavior, as indicated by our rheology results. This property facilitated the material's flow under applied pressure in the printer, effectively addressing processability issues. Moreover, the absence of debris, blobs, or irregularities in the printed layers led to cleaner, more precise prints with smoother surfaces and finer details. Additionally, the initial adhesion of the first printer layer to the printing bed was exceptional, indicating robust initial bonding and ensuring stable printing conditions throughout the entire job. This strong adhesion minimized the risk of warping, lifting, or detachment of the printed object from the build platform, thus preserving dimensional accuracy and print quality. It is noteworthy that the printed object exhibited negligible shrinkage, attributable to the incorporation of rigid biochar particles in the composite material, which contributed to the structural reinforcement of the printed object.

The high biochar content of 50 wt% achieved in this study is notable, especially considering that previous studies in material extrusion (MEX) 3D printing reported lower loadings before reaching saturation. For instance, biochar-filled acrylonitrile butadiene styrene composites were prepared as filaments compatible with material extrusion 3D printing, with biochar loadings up to 10.0 wt%. These filaments were used to print dog-bone specimens, and their mechanical properties were investigated [100]. Similarly, Vidakis et al. [101] explored different properties, including mechanical characteristics, of HDPE/biochar composites with biochar concentrations ranging from 2.0 to 10.0 wt%, printed using material extrusion techniques. This research group also developed a



Fig. 6. a) CAD design and b) the digital photograph of the printed object from various perspectives.

series of biocomposites using PLA and biochar for material extrusion applications. They observed a more than 20 % improvement in tensile strength at a 4 wt% loading compared to the pure PLA control sample [102]. In another study, up to 5 wt% biochar was blended with PLA to develop filaments suitable for material extrusion 3D printing, with optimization of printing parameters to enhance mechanical properties [60]. It is noteworthy that in most literature, the amount of biochar added in composites for material extrusion printing has been significantly lower compared to this work, where we utilized 50 wt% biochar. This difference can be attributed primarily to the method used to incorporate biochar into the PA12 matrix, i.e., in situ polymerization. This approach allows for a more intimate and effective dispersion of biochar within the polymer matrix compared to conventional methods, which typically involve melt blending. The in situ polymerization technique facilitates stronger interfacial interactions between biochar and PA12, thereby enabling the incorporation of higher biochar loadings while maintaining composite integrity and enhancing mechanical properties. This approach distinguishes this research by exploring the feasibility and potential advantages of using high concentrations of biochar in additive manufacturing, thereby providing novel insights into the field.

# 4. Key innovations and novel contributions

This section highlights the significant innovations and contributions of our study, underscoring its unique advancements in the field. The primary novelty of this work is the *in situ* polymerization of biochar with PA12, a pioneering approach that advances beyond traditional melt compounding methods. This technique allows for more effective dispersion of biochar within the PA12 matrix, which is a notable departure from conventional methods such as melt blending. The *in situ* polymerization process enhances interfacial interactions between biochar and PA12, thereby improving the dispersion and mechanical properties of the composite while maintaining its integrity.

Additionally, our study includes an LCA to demonstrate the reduction of  $CO_2$  emissions achieved by integrating biochar into the PA12 matrix. Another key innovation is the successful 3D printing of a highcarbon-content composite, which is significantly higher than previous studies reported in MEX 3D printing. This presents unique challenges in terms of material properties and printability.

These advancements underscore the study's contribution to reducing the environmental impact of traditional polymers and advancing the field of biochar-based composite materials for additive manufacturing. Furthermore, these promising results open several avenues for future research and development. For instance, detailed investigations into the long-term recyclability and environmental impact of these composites should be considered to validate their sustainability. Additionally, exploring the potential applications of PA12-biochar composites in various industrial sectors, such as automotive, aerospace, and construction, can provide valuable insights into their practical utility, especially in producing lightweight and durable components.

# 5. Conclusions

A series of composite materials, consisting of PA12 and biochar, were synthesized for the first time *via in situ* polymerization, marking a significant advancement in material engineering. The addition of biochar notably boosted the tensile strength and modulus of the PA12 composite. Specifically, these properties rose from  $38 \pm 1$  MPa and  $745 \pm 30$  MPa to  $54 \pm 2$  MPa and  $2055 \pm 65$  MPa, respectively, with the inclusion of 50 wt% biochar. Such enhancements underscore the effective dispersion of biochar within the PA12 matrix, emphasizing excellent compatibility between the polymer matrix and fillers. Morphological analysis, facilitated by SEM imaging, substantiated these findings, revealing no discernible crack formation, particle agglomeration, or phase separation. Furthermore, DSC and XRD analyses explained the

crystalline morphology of the composites, with biochar serving as nucleating agents, thereby augmenting crystallinity without significantly altering melting and crystallization temperatures. Additionally, TGA investigations affirmed the thermal stability enhancement conferred by biochar, evidenced by substantial increases in thermodegradation temperatures. Further insights into the viscoelastic behavior of the composites were garnered through DMA and rheological assessments, indicating heightened stiffness and viscosity attributable to biochar reinforcement, crucial for applications like 3D printing. The successful integration of biochar-enhanced polyamide composites in 3D printing applications underscores their practical viability and versatility in additive manufacturing. Moreover, a comprehensive LCA study revealed the climate change potential associated with biochar production from wood chips, ranging from -1.83 to +3.62 kg·CO<sub>2</sub>-equiv. per kilogram of material. When integrated into PA12 for structural applications, the net benefits stemming from biochar's biogenic CO2 sequestration were realized, yielding composite materials with a climate change potential ranging between 1.10 and 4.06 kg·CO<sub>2</sub>-equiv.·kg<sup>-1</sup>. Contextually, fossil-based nylon 6 and nylon 6-6 demonstrate substantially higher climate change potential values of 9.89 and 8.68 kg·CO<sub>2</sub>equiv.  $kg^{-1}$ , respectively. Furthermore, significant reductions in various environmental impacts, including eutrophication, particulate matter, material resource scarcity, and non-renewable CED, were observed with the introduction of biochar, further accentuating the environmental advantages of the developed composite materials. In summary, the observed improvements in mechanical strength, thermal stability, and viscoelastic properties, coupled with the excellent printability of the developed composites, alongside substantial reductions in various environmental impacts facilitated by biochar integration, hold significant promise for advancing sustainable engineering practices and meeting the evolving demands of various industrial sectors.

# CRediT authorship contribution statement

Hossein Baniasadi: Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. Erlantz Liizundia: Writing – review & editing, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. Zoe Paganelli: Formal analysis. Nele Dammann: Formal analysis. Lauri Välinen: Formal analysis. Jukka Seppälä: Writing – review & editing, Funding acquisition. Jukka Niskanen: Writing – review & editing, Supervision.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2024.111809.

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