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High-concentration lignin biocomposites with low-melting point biopolyamide

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ABSTRACT

Blending polymers with a high concentration of bio-based fillers is one of the solutions that not only reduces a dependency on petroleum-based feedstocks but can also significantly decrease the carbon footprint. In the current study, n-octadecyl isocyanate (ODI) molecules were grafted on lignin particles to render them compatible with a novel copolyamide matrix, which was successfully synthesized through a copolymerization between petroleum- and bio-based monomers. Different concentrations of the surface-modified particles were melt-blended with a low-melting point copolyimide, and the properties of the developed biocomposites being thoroughly studied. The SEM imaging revealed that the surface-modified particles homogeneously dispersed into the polymer matrix for all loading levels without any clear evidence of particle agglomeration, phase separation, or voids formation, proposing excellent compatibility between the components that arose from a successful surface modification process. Furthermore, the mechanical properties of the biocomposites significantly improved. For instance, the yield stress and tensile modulus were enhanced by 50% and 200% at the biocomposite with 50 wt% filler content, without any considerable change in the tensile strain. The dynamic mechanical analysis, as well as the rheology measurements, further confirmed the uniform dispersion of the surface-modified particles and their compatibility with the copolymer matrix, within which the storage modulus considerably improved upon the increase of filler content. Overall, our findings strongly suggest that these newly developed biocomposites with a green content of up to 80% are attractive candidates for substituting petroleum-based plastics for the demanded applications.

1. Introduction

Plastics are widely used in daily life due to their ease of processing, low cost, and low density. However, due to the depletion of sources as well as the environmental concerns arising from excessive consumption of polymers, such as global warming, an increased carbon footprint, and the effects on marine life, great efforts are being made to substitute these types of polymers with green, sustainable, and eco-friendly ones to fulfill the requirements of daily life [1–3]. Monomers derived from renewable biomass sources, such as vegetable oils, are mostly considered for developing green and sustainable polymers. They are abundantly available in nature with diverse structural features and are usually cheap as well as mostly non-toxic [4,5]. As one of the most promising vegetable oils, castor oil has been extensively used to develop partially and fully bio-based sustainable polymers, including polyurethanes, polyesters, and polyamides [6,7]. Polyamides, PAs, also known as nylons, are polymer families with high-performance properties, including superior mechanical strength, high stiffness/toughness, good thermal stability, and excellent resistance to a wide range of organic and inorganic solvents [8–10]. Polyamides are recyclable and, fortunately, can be synthesized from renewable biomass resources, such as castor oil. PA11, PA410, and PA1010 are clear examples of bio-based polyamides derived from castor oil-based monomers [11,12]. Thanks to the lower amide/methylene density in the backbone chain, these bio-based long-chain aliphatic polyamides not only present the aforementioned outstanding performance of traditional polyamides but also reveal a relatively low melting point, thus enabling further improvement of environmental impact by incorporating sustainable and bio-based fillers including cellulose, starch, sawdust, and lignin [13–15].

Lignin is the second most abundant bioorganic polymer after cellulose and the most abundant phenolic polymer on earth. As a by-product of the paper industry, lignin is considered a waste product; therefore, its utilization for unique applications has raised significant interest both scientifically and industrially. This high carbon content material is being...
en extensively used as a reinforcement material for polymer biocomposite production due to its abundant availability, sustainability, biodegradability, rigidity, and adequate thermal stability, as well as antibacterial and anti-oxidating activity [16–18]. Furthermore, it has been reported that using lignin as a filler reduces material costs [19,20]. Nevertheless, due to the hydrophobic nature of polyamides as well as the relatively less hydrophobic behavior of lignin arising from surface hydroxyl groups, the compatibility between the components would be somewhat challenging. In other words, incorporating lignin in a thermoplastic matrix, like PAs, may decrease the mechanical properties due to the inhomogeneous dispersion of lignin. Different chemical or physical approaches have been proposed to modify lignin characteristics, thereby enhancing its dispersibility and interface adhesion in two-phase composite systems. Namely, Muthuraj et al. [21,22] developed bio-based blends of different polyamides, i.e., ethylene–acrylic ester-maleic anhydride and ethylene-methyl acrylate-glycidyl methacrylate, to enhance the compatibility between the lignin and matrix. Accordingly, tensile strength and tensile modulus increased significantly; nevertheless, the elongation at break dropped dramatically. Furthermore, Atifi et al. [23] grafted different hydrophobic molecules, including cetyl trimethyl ammonium bromide, poly (ethylene oxide), polyethylene-block-poly(ethylene glycol), dodecenyl succinic anhydride, and alkyl ketene dimer on the surface of lignin to improve the adhesion and compatibility in polymer blends. They revealed that alkyl ketene dimer was the most efficient modifier molecule, changing the lignin from a hydrophobic particle to a hydrophobic one. As a result, the surface-modified lignin enhanced the stiffness of the polypropylene matrix by 15%. Moreover, lignin was chemically modified with poly(ethylene-co-glycidyl methacrylate) copolymer to incorporate into a low-density polyethylene matrix [24]. The authors revealed that interfacial adhesion between the lignin particles and the polymer matrix was better and more robust than that observed for the plain lignin particles, thereby introducing 20 wt% surface-modified lignin led to good quality lignin-reinforced polyethylene biocomposite. Hong et al. [25] applied a simple esterification reaction between lignin hydroxyl groups with anhydride molecules. The developed surface-modified lignin was incorporated into a polyactic acid matrix by a typical melt-mixing process. The obtained mechanical properties confirmed the interfacial adhesion performance between the treated lignin and matrix was better and stronger than pristine lignin.

To the best of the authors’ knowledge, only a few investigations are available in the literature concerning PA/lignin blends [17,20–22,26,27], most of which suffer from the poor flexibility of the final product. Thus, for the first time, we developed a series of lignin biocomposites, providing an excellent stiffness-toughness balance, even at a high filler loading of 50 wt%. We employed the same chemistry previously used for compatibilization of microcrystalline cellulose with a polyamide matrix [28], a urethane reaction between n-octadecyl isocyanate (ODI) molecules and the lignin hydroxyl groups. Accordingly, we converted lignin from a relatively hydrophilic particle into a hydrophobic one and made it compatible with the polyamide matrix. On the other side, to avoid any decomposition of lignin throughout the melt blending process, for the first time, we synthesized a bio-based copolyamide, PA11coPA1210, with a relatively low melting point of 158 °C and a green content of 63%. The copolymer was synthesized through a reaction between castor oil-based monomers, 11–aminoundecanonic acid and sebacic acid, and a petroleum-based monomer, 1,12-diaminododecane. The incorporation of the surface-modified lignin into the copolyamide matrix not only increased the green content to up to more than 80%, but also improved the matrix’s properties, proposing these renewable biocomposites competitive candidates for substituting traditional petroleum-based polymers.

2. Experimental

2.1. Materials

11-aminoundecanoic acid (97%), sebacic acid (99%), sodium hypophosphite monohydrate (greater than 99%), dibutyltin dilaurate (DBTDL, 95%), alkali lignin (low sulfonate content, impurities 4% sulfur, M_w = 10000 g mol^{-1}), n-octadecyl isocyanate (technical grade), trifluoroacetic anhydride (reagentPlus®, ≥99%), and chloroform-d (99.8% atom D) were purchased from Sigma-Aldrich. 1,12-diaminododecane was provided by Tokyo Chemical Industry. Chloroform (for analysis, EMPARTA® ACS) was obtained from Merck. Toluene (≥99.5%) was purchased from VWR and thoroughly dried before use. Ethanol (Etax B) was provided by Altia Industrial (Finland).

2.2. Copolymerization

The low-melting copolyamide was synthesized via a copolymerization reaction between fully bio-based PA11 and partially bio-based PA1210, as depicted in Scheme 1a. Sebacic acid and 1,12-diaminododecane were selected as a precursor of PA1210, while 11-aminoundeca-noic acid was considered for PA11 synthesizing. An identical mole of the monomers and 1 wt% catalyst (sodium hypophosphite monohydrate) were introduced to a stainless-steel reactor. The reactor was purged with nitrogen gas for 10 min and then heated up to 200 °C for the monomers to melt. Afterward, the temperature was increased to 240 °C, and the system was stirred at 15 rpm for 4 h under a vigorous nitrogen flow to ensure efficient removal of the by-product, that is, water vapor. The reactor was cooled down using an ice bath under the nitrogen flow to work up the reaction. The plain PA11 and PA1210 were synthesized using the same method.

2.3. Lignin surface modification

The lignin particles were modified by changing the particles’ surface from hydrophilic to hydrophobic through a urethane reaction between isocyanate molecules and lignin hydroxyl groups due to the method reported in our previous work [28]. A schematic representation of this reaction is depicted in Scheme 1b. The reaction was carried out in a three-neck round-bottom glass reactor, previously loaded with thoroughly dried lignin particles. Under the nitrogen flow, dried toluene and some drops of DBTDL as a catalyst were added to the reactor. When the temperature reached 90 °C, ODI was added drop-by-drop. The reaction was maintained at the same temperature for 8 h. Subsequently, the surface-modified lignin was filtered and washed several times with ethanol to remove any un-reacted isocyanate molecules as well as any amine formed during the reaction. The produced surface-modified particles were thoroughly dried and then placed in a desiccator prior to blending with the copolyamide.

2.4. Melt-blending and sample preparation

The synthesized copolymer and the surface-modified lignin particles were melt-blended in a twin-screw micro-compounder (DSM, The Netherlands). Different weight ratios of each dried component were physically mixed and, in turn, fed to the extruder. The blending temperature was set at 200 °C, while the rotating speed was 20 rpm to provide a residence time of 5 min inside the cavity: This time, experimentally obtained, ensured efficient mixing of two components without facing any considerable thermal degradation of lignin particles. The extruder output was then cut into small pieces using a pelletizer and fed into an injection-molding machine (Babyplast 6/10P, England) to prepare dog-bone samples for the tensile testing. The film-shape samples were also prepared using a lab press (Fontijne Lab Press – TP 400, The Netherlands). Both injection molding and hot-pressing processes were implemented at 200 °C. The portion of copolyamide and surface-
modified lignin particles were selected as 90/10, 80/20, 70/30, 60/40, and 50/50 (w/w), respectively. Therefore, the biocomposites were designated as PA-SMLig10, PA-SMLig20, PA-SMLig30, PA-SMLig40, and PA-SMLig50, respectively. It is worth noting that, considering the bioccontent of the copolymer itself, which was approximately 64 %, the green content of the biocomposites rose to 82 %, contributing considerably to the carbon footprint reduction.

2.5. Characterization

2.5.1. Fourier transform infrared spectroscopy, FTIR

The chemical structure of the lignin before and after surface modification, as well as the synthesized plain PA11 and PA1210 and their copolymer, were investigated using a PerkinElmer ATR FTIR machine. The spectra were recorded between 4000 and 500 cm\(^{-1}\) with a 4 cm\(^{-1}\) resolution and a scan rate of 16.

2.5.2. Proton nuclear magnetic resonance spectroscopy, \(^{1}\text{H NMR}\)

\(^{1}\text{H NMR spectroscopy was performed on PA11, PA1210, and the copolymer to further investigate their chemical structure. A diluted sample solution in a mixture of chloroform-d and trifluoroacetic anhydride (90/10, v/v) was prepared before examination with a Bruker NMR Spectrometer model AV III 400.}

2.5.3. Gel permeation chromatography, GPC

The number and weight average molecular weights, as well as the polydispersity index of the PA11, PA1210, and the copolyamide, were measured by a gel permeation chromatography method using a GPC machine model Waters Whyatt Mills model 717 plus Autosampler, USA. A mixture of chloroform-d and trifluoroacetic anhydride (90/10, v/v) was used as a solvent for the samples and polystyrene standards.

2.5.4. Elemental analysis

The elemental analysis was carried out using a Thermo FlashSmart
CHNSO Elemental Analyzer, USA. The amounts of carbon (C), oxygen (O), hydrogen (H), nitrogen (N), and sulfur (S) elements were measured before and after surface modification to ascertain the successful grafting of ODI molecules with the lignin particles.

2.5.5. Scanning electron microscopy, SEM

Lignin particles’ morphology before and after surface modification was assessed by SEM imaging, performed by a TESCAN machine model Mira3. The powder was coated by a thin layer (~4 nm) of gold and palladium prior to the subjection of SEM imaging. The degree of dispersion of lignin particles into the copolyamide matrix was also monitored by SEM images. The sample was first broken in liquid nitrogen and then coated with a thin gold–palladium layer (~4 nm) before imaging at an accelerating voltage of 5 kV.

2.5.6. Differential scanning calorimetry, DSC

The melting point and crystallinity of the plain PA11, PA1210, and the copolyamide were examined with a DSC machine model TA Instruments MT-DSC Q2000. The temperature range and the heating/cooling rate were 0 to 250 °C and 10 °C·min⁻¹, respectively. All samples were first heated and then cooled under a nitrogen atmosphere to remove their thermal history; after this, the second cycle was performed to investigate the samples’ melting point (Tm), crystallization temperate (Tc), melting enthalpy (ΔHm), and crystallization enthalpy (ΔHc). The melting enthalpy was used to calculate the degree of crystallinity of the samples (χc) by Eq. (1).

\[
χ_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100
\]  

where ΔHm is the melting enthalpy of 100 % crystallized sample. It was 226.4 J·g⁻¹ for PA11 [29]. To the best of the authors’ knowledge, there is no value for the melting enthalpy of a 100 % crystallized PA1210 in the literature; therefore, the reported value for PA1012 (209.2 J·g⁻¹) [22] was considered since this polyamide has the same carbon number in the repeating unit and has the closest structure to PA1210. Furthermore, the melting enthalpy of a 100 % crystallized copolymer was calculated considering the weight percent of each component, that is, PA11 and PA1210, in the copolymer (Eq. (2)). Since an identical mole of each monomer was used for copolymerization, the weight percent of PA11 and PA1210 in the copolymer was 33.34 % and 66.66 %, respectively.

\[
\Delta H_m^{\text{copolymer}} = 0.34\Delta H_m^{\text{PA11}} + 0.66\Delta H_m^{\text{PA1210}}
\]  

2.5.7. Thermogravimetric analysis, TGA

The thermal degradation behavior of the samples was studied using a TA instrument model Q500 under a nitrogen atmosphere between 30 and 800 °C with a heating rate of 10 °C·min⁻¹. The thermograms were used to investigate the amount of ODI grafting on lignin particles qualitatively.

2.5.8. Tensile test

The tensile test was performed on ISO 27-2 standard specimen type 1BB. The samples were first conditioned in a relative humidity of 50 % and temperature of 23° for 48 h. They were stretched with a tensile speed of 5 mm·min⁻¹ under a 2 kN load cell using a Universal Tester Instron machine mode 5944. The force–displacement data was used to draw the stress–strain curves. Accordingly, tensile modulus, yield stress, elongation at break, and tensile strength were extracted from the curves. The sample toughness was considered the area under the stress–strain curve (J·m⁻²). The reported values were the average of three measurements ± standard deviation.

2.5.9. Dynamic mechanical analysis, DMA

The DMA was used to investigate the degree of surface-modified lignin particle dispersion in the copolymer matrix by monitoring the changes of storage modulus (E’) and loss modulus (E”) over temperature. The test was carried out between 30 and 160 °C with a heating rate of 5 °C·min⁻¹ using a TA Instruments model Q800. The test was performed in low deformation (1 % strain) to guarantee that the measurements were in the linear viscoelastic range. Furthermore, the pre-load and frequency were fixed at 1 N and 1 Hz, respectively [28]. The maximum loss factor (tan δ) curve was also considered to be the glass transition temperature (Tg) of the samples.

2.5.10. Rheology

The viscoelastic properties of the samples as an efficient tool for studying the compatibility between two phases, that is, the copolymer matrix and the particles, were assessed by rheology testing. The oscillatory measurements were performed on the disk-shaped sample (diameter of 25 mm) at 200 °C employing an Anton Paar Physica rheometer model MCR 301 equipped with a PP25 geometry. The sample was first punched into a disk shape with a diameter of 25 mm. The linear viscoelastic region, in which storage (G’) and loss (G”) moduli were independent of strain rate, was found via a strain sweep test between 0.01 and 100 % at a fixed angular frequency of 1 Hz. After that, a frequency sweep test was conducted at a fixed strain rate of 10 %, between angular frequency of 0.01–100 Hz, to investigate the trend of G’ and G” upon the addition of surface-modified lignin particles. The effect of particles addition on the complex viscosity (|η’’|), which was obtained from the frequency sweep test, was also followed.

3. Results and discussion

3.1. Lignin particles surface modification

Hydrophilicity is one of the limitations of lignin-based materials for blending with polymer materials like polyamides. The grafting of long-chain hydrocarbons and, thereby, changing lignin from a hydrophilic particle into a hydrophobic one is one of the well-known solutions to overcome this drawback and enhance interfacial adhesion and compatibility between polymer matrix and filler [30,31]. In the current study, the hydrophobization of the lignin was implemented through the grafting of aliphatic isocyanate molecules, i.e., ODI, which has a close structure to the matrix, i.e., long-chain aliphatic polyamide. The successful attachment of the ODI molecules on lignin particles was investigated using elemental analysis, FTIR spectra, and TGA/DTG thermograms. Table 1 presents the elemental analysis results for plain lignin and surface-modified one. There was a significant difference between the elements of C, H, N, S, and O for lignin and surface-modified lignin. Although the amount of N in the lignin sample was not in the range that the instrument could detect, the surface-modified one showed approximately 0.5 % nitrogen content, suggesting the presence of the molecules with, for instance, the nitrogen atom, ODI. Furthermore, the amounts of C, O, and H elements significantly changed in the surface-modified sample, illustrating the presence of the external molecules in the lignin particles. The amount of attached ODI molecules was previously reported for cellulose [28,32]; however, since the exact structure of the lignin is not clear, it was not possible to quantify the exact percentage of the grafted ODI molecules for the surface-modified lignin particles.

| Sample         | Carbon (C) (%) | Oxygen (O) (%) | Hydrogen (H) (%) | Nitrogen (N) (%) | Sulfur (S) (%) |
|----------------|---------------|----------------|------------------|-----------------|----------------|
| Lignin         | 47.99         | 31.74          | 4.57             | 0               | 1.83           |
| Surface-modified lignin | 51.74         | 28.30          | 5.25             | 0.47            | 0.47           |
The TGA/DTG thermograms were used to qualitatively evaluate the attachment of the modifier molecules. The TGA/DTG thermograms of lignin before and after surface modification are illustrated in Fig. 1a. Lignin displayed three distinct weight loss regions; the first one appeared below 200 °C, corresponding mainly to water release; the second one between 200 and 550 °C with a broad DTG peak at 320 °C assigned for major devolatilization reactions; and finally, a minor weight loss above 550 °C attributed to the decomposition of the most thermally stable organic matter [33]. The thermal decomposition stages were repeated for the surface-modified lignin particles; in addition, one new weight loss region appeared between 200 and 300 °C, accompanied by a DTG peak at 270 °C. It has been shown that most of the aliphatic molecules thermally decompose in the range of 200–300 °C [10]; therefore, the appearance of this peak could be associated with the decomposition of ODI molecules attached to lignin particles. It is worth noting that the maximum thermal degradation of lignin shifted towards a higher temperature, from 320° to 345 °C, in the surface-modified sample, which has been attributed to the increase in the crystallinity of the sample after surface modification [34,35]. Furthermore, the weight loss percentage below 200 °C was considerably lower in surface-modified lignin than in the plain sample, which could be explained by less hydrophilicity of the sample due to the reduction of hydroxyl groups that reacted to ODI molecules. It is to be remarked that due to the thermal sensitivity of the modifier molecules, the relatively lower melting point of the newly developed copolyamide rather than the commercially available ones, PA11, for instance, could be advantageous; otherwise, most of the ODI molecules decomposed at a very high extruding temperature.

The FTIR spectra were used to study the chemical bond between the lignin particles and ODI molecules. The results are illustrated in Fig. 1b. The plain lignin samples illustrated a series of peaks in the range of 1510 cm\(^{-1}\) to 1410 cm\(^{-1}\), corresponding to the aromatic ring vibrations of the typical phenyl propane units [36,37]. The surface-modified samples revealed the same peaks, suggesting that the surface modification did not change the chemical structure of the lignin. Furthermore, some new peaks could be detected, proving the attachment of the ODI molecules on lignin particles; asymmetric and symmetric methylene groups of the grafted alkyl chain at 2920 cm\(^{-1}\) and 2840 cm\(^{-1}\) regions, and amide I and amide II vibration peaks at 1610 cm\(^{-1}\) and 1575 cm\(^{-1}\), respectively. The proper removal of ODI molecules after the washing process was confirmed by the absence of any characteristic peaks in the region of 2270 cm\(^{-1}\), which is assigned to the isocyanate groups [28,32].

The morphology of the lignin particles was studied by SEM imaging to investigate the harshness of the modification process. The SEM images of lignin particles before and after surface modification are provided with two magnifications in Fig. 1c-f. The lignin particles had irregular shapes with varying particle sizes, which were in the range of a few ten microns. Furthermore, the surface of the particles was smooth and intact. The particles’ size and shape did not change considerably after the modification process; however, dent structures and noticeable roughness could be observed. It is noteworthy that no clear white spots, holes, or any obvious defect could be seen on the surface of treated samples, suggesting that the ODI surface modification was mild and non-destructive, and it was done in nanoscales [38,39]. Of note, the rougher surface of the lignin particles after treatment could be advantageous when blending with polyamide because a higher surface area would be available.

3.2. Low-melting point copolyamide characterization

One of the targets of the current study was to synthesize a bio-based polyamide with a relatively low melting point suitable for blending with bio-based fillers, such as lignin. It has been reported that copolymerization is an effective method for reducing the melting point of polyamides acting on the regularity of the polymer chain [40]. Accordingly, the copolymerization of fully bio-based PA11 and partially bio-based PA1210 was reported and investigated for the first time. The successful copolymerization was thoroughly examined and confirmed via FTIR, \(^1^H\) NMR, GPC, TGA, and DSC techniques, as discussed in the following sections.
The chemical structure of the synthesized PA11, PA1210, and copolyamide were investigated using FTIR and 1H NMR spectra to confirm the successful synthesis of the samples through polycondensation reaction between the employed monomers. The results are depicted in Fig. 2a and b. All the synthesized samples presented typical FTIR characteristic peaks of polyamides reported in the literature [41,42]. There were as follows: a peak at 3297 cm\(^{-1}\) assigned for the N–H bond, two sharp peaks at 2930 cm\(^{-1}\) and 2850 cm\(^{-1}\), respectively, attributed to CH\(_2\) asymmetric and symmetric stretch; two peaks at 1640 cm\(^{-1}\) and 1545 cm\(^{-1}\), respectively, corresponded to amide I (stretch C=O) and amide II (–NH-CO–), a peak at 1466 cm\(^{-1}\) due to C–O bending, and a peak at 945 cm\(^{-1}\) arose from amide IV. On the other hand, the signals in the 1H NMR spectra were in line with those reported for polyamides in the literature. For instance, two signals at 3.7 ppm and 2.8 ppm were attributed to the methylene proton adjacent to amino and carbonyl groups, respectively. Furthermore, the 1.3–1.6 ppm signals were assigned to the methylene proton in aliphatic chains [9,14,15]. The appeared peaks at 7.3 ppm and 10.4 ppm were assigned to chloroform-d trifluoroacetic anhydride solvents, respectively [14].

To further investigate the polymerization process as well as the possibility of any side-product formation during the copolymerization, the GPC testing was run, and the number average and weight average molecular weight (Mn and Mw ), as well as the polydispersity index (PDI) of the samples being measured. The results are summarized in Table 2. The GPC curves are also provided in Fig. S1. The plain polyamides, as well as the copolymer sample, presented a unimodal narrow molecular weight distribution with a number average molecular weight between 47,000–52,000 g mol\(^{-1}\), proposing that the composition was relatively simple and no copolymers with different sequence structures were formed during copolymerization. Although the plain PA11 and PA1210 had the longest building blocks, the dispersity in the copolymer was relatively lower than their parents, suggesting that the copolymerization was even more well-controlled in contrast to the plain polyamides polymerization [43,44]. To further confirm the absence of any side-product formation during the copolymerization, the thermal degradation behavior of the plain PAs and the copolymer was examined. The TGA/DTG thermograms of the samples are provided in Fig. 2c, in which PA11 and PA1210 illustrated a typical polyamides degradation mechanism: a constant weight before 400 °C, followed by entire decomposition between 400 and 500 °C with a single maximum thermal degradation peak at approximately 460 °C [45]. The copolymer also presented the same degradation behavior as their parents, which could be another piece of evidence of the absence of different active centers during copolymerization.

DSC scans of the synthesized copolymer and its parents, that is, PA11 and PA1210, are depicted in Fig. 2d. In addition, the melting point, crystallization temperature, crystallization enthalpy, melting enthalpy, and crystallinity are provided in Table 2. All samples presented a single melting and crystallization temperature, indicating one crystal type formation during polymerization, such as alpha crystalline form [46]. The crystallization temperature and melting point of the synthesized PA11 were in line with those reported in the literature. In the case of PA1210, these temperatures were similar to the reported values for PA1012, which has the same carbon number per repeating unit [47,48]. The copolymer crystallized and melted at a relatively lower temperature than its parents. However, the crystallization enthalpy, melting enthalpy, and crystallinity were significantly lower in copolymer than the plain PA11 and PA1210. In other words, although the crystals

![Fig. 2. a) FTIR, b) 1H NMR, c) TGA/DTG, and d) DSC of PA11, PA1210, and copolymer.](image-url)
formed earlier in the copolymer, the interaction between the different monomers led to enlarged supramolecular structures, thus hindering the formation of large polyamide crystalline regions [22]. A similar observation has been reported for the copolymerization of PA11 and PA12 [28,40].

3.3. Biocomposites characterization

Uniform dispersion of the fillers, as well as their excellent interaction with the matrix, are two critical keys governing the properties of the composites. Therefore, different techniques were used to evaluate the lignin particles’ distribution into the copolymer matrix and, consequently, its effect on the mechanical performance of the developed biocomposites.

3.3.1. Morphology

The SEM imaging was performed from the cryofracture surface of the biocomposites with different surface-modified lignin content. The results are presented in Fig. 3. Furthermore, the SEM image of the biocomposite containing 30 wt% untreated lignin is provided in Fig. 3 for comparison. On the one hand, the surface-modified lignin particles homogeneously dispersed in the copolymer matrix for all loading content, while the particles sizes in each composition were approximately similar to that previously observed for the plain lignin particles (Fig. 1), suggesting that the particles were not broken down too much during the blending. On the other hand, no evidence of phase separation, agglomeration, or void formation could be detected, proposing good compatibility between components, even at a high loading of 50 wt%. Although poor component adhesion could be seen in a composite sample containing 30 wt% untreated lignin particles, the particles were well-mixed with the polymer matrix and presented good adhesion in all the biocomposites prepared by surface-modified lignin; therefore, the polymer matrix partially covered the surface of the particles. Other researchers also reported a relatively homogeneous distribution of surface-modified lignin particles in different polymer matrices; however, to the best of the authors’ knowledge, very few studies demonstrated such a uniform particle distribution even at a high filler loading of 50 wt%, which can be the superiority of the current work in between. For instance, Muthuraj et al. [22] observed a heterogeneous morphology with just up to 20 % of filler content. In contrast to the current study, in most of the earlier research work carried out on polymer/lignin blending, a significant reduction has been reported in elongation at break and, consequently, in toughness on increasing the bio-filler content even for surface-treated lignin particles. This behavior has been attributed to the reduced mobility of the polymer chains obtained by the strong filler-filler interactions and incorporation of rigid lignin moiety in the matrix that caused the composites to become more brittle [19,30]. It has also been ascribed to the aggregation of the lignin particles due to polar functional moiety in the lignin structure, resulting in poor compatibility between the components [11,51]. For instance, Szabo et al. [52] observed heterogeneous phase morphology with large lignin domains in the polypropylene matrix, which resulted in poor mechanical performance. Similarly, Atif et al. [23] reported poor mechanical properties for poly(ethylene oxide)-treated lignin/polypropylene composites, which was attributed to the poor dispersion of the treated lignin particles into the polymer matrix. Although significant improvement has been achieved by the incorporation of 5 wt% silylated lignin and 2 wt% kraft lignin, respectively, in the rubber [30] and bisphenol A glycerolate/diacrylate/ethylene glycol dimethacrylate [19] matrices, a further increase in the treated lignin loading resulted in the reduction of the mechanical properties attributed to the aggregation of lignin particles and poor lignin-matrix interactions. In the current study, it is notable that the improvement of the mechanical properties was obtained at up to 40 wt% lignin loading, which strongly supports the benefit of the employed treatment method for compatibilizing lignin particles with polymer matrices.

3.3.2. Mechanical properties

The typical stress–strain curves obtained from the tensile testing are presented in Fig. 4a. Furthermore, tensile modulus, yield stress, tensile strength, tensile strain or elongation at break, and toughness of the samples are also provided in Fig. 4b and Table S1. The tensile modulus and yield stress significantly improved upon increasing the surface-modified lignin particles. The former was enhanced by 800 %, and the latter improved by 50 %, as previously confirmed by SEM images, suggesting excellent compatibility between the components and uniform dispersion of particles inside the polymer matrix, which further facilitated the transfer of applied stress among matrix and lignin particles, resulting in superior mechanical properties. The gain in tensile modulus could also be explained by the higher intrinsic stiffness of lignin particles rather than the copolyamide matrix, as well as stronger filler-filler interactions [30,50]. On the other hand, the tensile strength and strain remained the same or slightly increased, except for the biocomposite being filled with 50 wt% filler. This could be due to the lack of voids and substantial wetting that arose from excellent compatibility and inter-action between the filler and polymer matrix, hindering crack propagation when the samples underwent a tensile strain [11]. The reduced tensile strength and strain in the PA-SMLig50 sample could be explained by the partial agglomeration of particles at such a high loading content. In other words, 50 wt% could be considered a threshold for surface-modified lignin particles loading in the synthesized copolymer matrix.

In contrast to the current study, in most of the earlier research work carried out on polymer/lignin blending, a significant reduction has been reported in elongation at break and, consequently, in toughness on increasing the bio-filler content even for surface-treated lignin particles. This behavior has been attributed to the reduced mobility of the polymer chains obtained by the strong filler-filler interactions and incorporation of rigid lignin moiety in the matrix that caused the composites to become more brittle [19,30]. It has also been ascribed to the aggregation of the lignin particles due to polar functional moiety in the lignin structure, resulting in poor compatibility between the components [11,51]. For instance, Szabo et al. [52] observed heterogeneous phase morphology with large lignin domains in the polypropylene matrix, which resulted in poor mechanical performance. Similarly, Atif et al. [23] reported poor mechanical properties for poly(ethylene oxide)-treated lignin/polypropylene composites, which was attributed to the poor dispersion of the treated lignin particles into the polymer matrix. Although significant improvement has been achieved by the incorporation of 5 wt% silylated lignin and 2 wt% kraft lignin, respectively, in the rubber [30] and bisphenol A glycerolate/diacrylate/ethylene glycol dimethacrylate [19] matrices, a further increase in the treated lignin loading resulted in the reduction of the mechanical properties attributed to the aggregation of lignin particles and poor lignin-matrix interactions. In the current study, it is notable that the improvement of the mechanical properties was obtained at up to 40 wt% lignin loading, which strongly supports the benefit of the employed treatment method for compatibilizing lignin particles with polymer matrices.

3.3.3. Dynamic mechanical properties

DMA testing was performed to understand further the microstructure and the interfacial adhesion between the surface-modified lignin particles and copolymer matrix, as well as to investigate the dynamic mechanical properties of the samples. The storage (E’) and loss moduli (E’’), as well as the loss factor (tan δ) of the plain copolymer and biocomposites with different lignin loading, are shown in Fig. 4c and d. Both E’ and E’’ significantly increased on increasing the lignin content over the entire experimental temperature; however, it was more dominant at lower temperatures. For instance, E’ increased from 610 MPa in the plain matrix to 1450 MPa in the biocomposite containing 50 wt% surface-modified lignin, at 30 °C. This improvement could be explained by the homogeneous dispersion of stiff and rigid lignin particles with complex structures into the polymer matrix, good interfacial adhesion between the matrix and the nanofiller, and the strong filler-filler interactions which constrained the motion of polyamide chain segments [30,53,54]. All the samples experienced a dramatic decrease of about

### Table 2

| Sample      | Mn (g mol\(^{-1}\)) | Mw (g mol\(^{-1}\)) | PDI | T\(_{m}\) (°C) | \(\Delta H_{m}\) (J g\(^{-1}\)) | T\(_{g}\) (°C) | \(\Delta H_{g}\) (J g\(^{-1}\)) | \(\chi_C\) (%) |
|-------------|---------------------|---------------------|-----|---------------|-------------------------------|---------------|-------------------------------|----------------|
| PA11        | 52,000              | 108,000             | 2.08| 166           | 42.59                         | 190           | 34.62                         | 15.3           |
| PA1210      | 52,000              | 116,000             | 2.23| 173           | 53.40                         | 187           | 51.98                         | 24.85          |
| Copolymer   | 47,000              | 87,000              | 1.85| 116           | 32.32                         | 158           | 28.2                          | 13.11*         |

* The melting enthalpy of 100 % crystalline copolymer was considered 215.05 J g\(^{-1}\) due to Eq. (2).
Fig. 3. Cross-sectional SEM images of a) PA-SMLig10, b) PA-SMLig20, c) PA-SMLig30, d) PA-SMLig40, e) PA-SMLig50, and f) PA-Lig30.
two orders of magnitude in the range of 50–70 °C, associated with the glass transition relaxation of the polymer chains. They presented a peak on tan δ curves at this temperature range, known as a glass transition temperature (Tg). Below this temperature range, the movement of the chain segment was restricted since the samples were in a glassy state, and as a result, E’ was high. Change from a glassy to a rubbery or high-elastic state happened after Tg, caused the chain segment to gradually recover its motion ability, and E’ rapidly decreased. It is worthy of mention that the tan δ peak height was higher in the biocomposites, thus indicating the higher damping properties due to the physical nature of the lignin and implying that lignin had good compatibility with the polymer matrix [16,55]. Furthermore, the presence of a well-defined peak in the loss factor has been considered another piece of evidence indicating a homogeneous microstructure of the blend and the miscibility of the components [54].

3.3.4. Rheology
The rheology testing was conducted in oscillatory mode to further assess the filler-filler and filler-polymer interactions as well as to acquire more information about the processing characteristics of the biocomposites [30,54]. Fig. 5 demonstrates the storage modulus (G’), loss modulus (G’’), loss factor (tan δ), and the complex viscosity of the plain copolymer and biocomposites with different lignin loading. First, the strain sweep tests were performed at 200 °C under a fixed angular frequency of 1 Hz to find the linear viscoelastic region. The results are depicted in Fig. 5a. All samples revealed an independent trend at low shear strain rates, known as linear viscoelastic behavior, followed by a descending trend at higher shear rates, similar to that reported in the literature. The linear viscoelastic region was wider in biocomposites rather than the plain matrix, except in the PA-SMLig50 one, indicating the formation of well-preserved networks established by good filler-polymer and filler-filler interactions, which stood more against deformation. The different behavior of the PA-SMLig50 sample could be due to the partial aggregation of lignin particles at a high loading of 50 wt%, as previously proposed by the tensile testing results. Overall, a shear strain of 10 % was chosen as the safe strain value, guaranteeing that the measurements were in the linear viscoelastic region. To further study the dispersion level of particles into the polymer matrix and their interaction, the frequency sweep tests were performed within the linear viscoelastic region at 200 °C, in which the angular frequency rose from 0.1 to 100 rad s$^{-1}$ (Fig. 5b). For all the samples, both G’ and G’’ increased as angular frequency increased, while G’’ was greater than G’ throughout the frequency range; therefore, the loss factor, the ratio of G’’ and G’ (Fig. 5c), was always higher than 1, indicating that the viscosity of the samples was greater than their elasticity [56,57]. In other words, all samples showed a high viscous response in the molten state, in which the polymer chains were fully relaxed, and the samples behaved as liquid-like material rather than solid-like material. Although the moduli increased upon increasing filler content, especially at lower frequencies, all biocomposites predominantly behaved as fluids in the test conditions in contrast to the previous report [22], in which cross-linking of the lignin particles at a high filler loading of 50 wt% has been observed (G’’ intersected G’ curves). The improvement of the moduli could be due to the compatible surface-modified lignin particles evenly dispersing and forming interconnected networks as well as strong interfacial interaction with the matrix, and accordingly restraining the movement of macromolecular chains during the applied shear force [54,56,58]. Nevertheless, they never caused any crosslinking; therefore, the residence time control for avoiding or minimizing the possible crosslinking during blending is no longer a concern.

Fig. 4. a) The stress–strain curves and b) the comparison of the mechanical properties of the copolymer and biocomposites. c) Storage (solid symbols) and loss (blank symbols) moduli and d) tan δ of the copolymer and biocomposites.
The particles’ dispersion, as well as their adhesion with the polymer matrix, were further evaluated by monitoring the complex viscosity behavior versus frequency. The results are depicted in Fig. 5d. The viscosity revealed a systematic reduction over frequency, indicating a non-Newtonian trend known as shear-thinning behavior, which could be an advantage for melt-processing. This behavior could be explained by the destruction of networks or the lack of time for polymer chains to orient themselves with the applied forces at higher frequencies [9,28]. On the other hand, the complex viscosity was enhanced by the increase in the filler content, proposing the formation of robust networks through polymer-filler and filler-filler interactions, achieved by even dispersion of the lignin particles into the matrix and good compatibility between the components, resulting in the long-range polymer chain relaxation being restrained and the structure being preserved well under the applied stress [59]. The formation of additional chain entanglements between polymers in the presence of lignin particles, which reduced the macroscopic fluidity [56], could be another evidence of increased viscosity upon filler-loading.

4. Summary and future perspective

Polymers are ubiquitous in our daily lives, which can be found in simple household objects like food packages or on more sophisticated materials like biomedical or electronics devices. They are mainly produced from fossil origin, thus, raising severe pollution and climate changes issues. Hence, the scientific community has been conducting an ongoing search for viable renewable alternatives to petroleum-based products. Biomass feedstocks, such as plant oils, fatty acids, cellulose, and lignin, have been considered potentially sustainable alternatives to producing polymers [60–62]. In this context, lignin has been deeply studied for its potential integration into different new materials as a sustainable replacement for some petroleum derivatives and chemicals [63,64]. Likewise, castor oil has been introduced as a promising source for developing several renewable and sustainable polymers such as polyurethanes, polyesters, epoxy-polymers, and polyamides [65,66]. In the current study, we proposed a series of biocomposites consisting of low-melting point biopolyamides and lignin particles with excellent stiffness-toughness balance as renewable plastics for substituting petroleum-based polymers. Although most of the raw materials were obtained from renewable and sustainable resources, i.e., castor oil and lignin, a comprehensive life cycle assessment study will be required to thoroughly investigate the sustainability of the developed bio-composites, as well as their total environmental impact.

5. Conclusion

A series of green and bio-based composites were successfully developed by blending a novel low-melting point copolyamide with surface-modified lignin particles. The copolyamide was synthesized for the first time through a copolymerization reaction between castor oil-based monomers, that is, 11-aminoundecanoic acid and sebacic acid, and a petroleum-based monomer of 1,12-diaminododecane. The successful
synthesis was evaluated and confirmed. The copolyamide was then melt-blended with different loading of surface-modified lignin particles. The surface modification of the lignin particles, which was modified based on the grafting of \( \text{n-octadecyl isocyante} \) molecules, improved the particles’ compatibility with the polymer matrix. SEM imaging from the cryofracture surface area of the biocomposites confirmed homogenous dispersion of surface-modified particles into the matrix, as well as the excellent compatibility between the components through the absence of any phase separation or voids formation. The uniform distribution of the surface-modified particles was further observed in the mechanical testing results, in which the mechanical properties significantly improved even at a high filler loading of 50 wt%. Furthermore, the dynamic mechanical measurements and rheology results provided evidence of good filler-filler and filler-matrix interactions, causing improved even at a high filler loading of 50 wt%. Furthermore, the dynamic mechanical measurements and rheology results provided evidence of good filler-filler and filler-matrix interactions, causing considerable improvement in the storage modulus of the biocomposites. To summarize, our results introduced these newly developed eco-friendly biocomposites with a green content of up to 80 % as a competitive material for substituting petroleum-based plastic for the demanding engineering applications.

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

No data was used for the research described in the article.

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Appendix A. Supplementary data

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