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Thermoplastic lignocellulose materials: A review on recent advancement and utilities

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ABSTRACT

Lignocellulosic biomass is the most abundantly available resource in nature. However, its potential as a replacement of oil in plastic production has not been fully exploited. To reduce the carbon footprint, the use of lignocellulose biomass to produce bio-based plastics is attracting increasing global interest. The aim of this review article is to systematically summarize the recent advancements of the development of lignocellulose materials that possess thermoplastic properties, meaning they can be processed/shaped by common plastic processing techniques. The approaches used for modification of lignocellulose biomass and the properties of the modified materials, as well as factors affecting the properties of these, are discussed. The regulatory aspects and policy directions of bio-based plastics, including thermoplastic lignocellulose, are also mentioned. Current challenges of producing thermoplastic lignocellulose and the way forward to solve this are also explored.

1. Introduction

Plastics are one of the most widely used materials globally, almost in all spheres of life from packaging, electronics, automotive, household materials, to building and constructions materials (Allin, 2004). At the same time, it pollutes all spheres of the earth, from the deep sea to the uppermost atmosphere, causing pollution and burden on the planet, through littering and incineration. If the current scenario of plastic production continues, the amount of plastics produced is estimated to reach 12 billion tons by 2050 (Geyer et al., 2017). From 1950–2015, an estimated amount of 8.3 billion tons of virgin plastics were produced in the world, generating 6.3 billion tons of plastic waste from which 0.6 billion tons have been recycled, about 0.8 billion tons incinerated, while the remaining 4.9 billion tons (79%) have been released to the environment (Geyer et al., 2017).

Fig. 1 shows the production trends of fossil-based plastics and associated environmental impacts. The environmental impact and resource limitedness of fossil fuel-based products have led to a search for sustainable and environmentally friendly substitutes (Miller, 2013; White & Lockyer, 2020). In recent years, the impact of plastics on the environment has been in focus and increasing levels of pollution are mainly caused by the increased consumption, driven by the growing population and improved levels of economy and living standards in developing countries (Barnes, 2019; Dilkes-Hoffman et al., 2019; Litchfield et al., 2020; White & Lockyer, 2020). This has resulted in a paradigm shift regarding the public opinion, as well as changes in government regulations, towards a possible replacement of fossil fuel-based plastics and an increasing momentum for bio-based plastics (Dilkes-Hoffman et al., 2019; EU (COM), 2019; Pacala & Socolow, 2004; Ragauskas et al., 2006; Suzuki et al., 2021; White & Lockyer, 2020). Consequently, large research efforts are focused on switching from fossil-based to bio-based plastics. Even if the need for sustainable and renewable product is increasing, the market share of bio-based products is still very limited. In 2018, Germany's Nova Institute revealed that biobased polymers (biopolymers) contribute with only 2% of the total annual production of fossil-based plastics, i.e. about 7.5 million tons, which is anticipated to grow by 4% till 2023 (Chinthapalli et al., 2019). The need for bio-based plastics is high, however, the low cost of fossil-based plastics and the lack of regulations (encouraging the production of bio-based plastics and discouraging the use of fossil-based plastics) are hindering the transition to bio-based polymers. Thermoplastic lignocellulose is among the most interesting alternative to conventional fossil-based plastics.

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However, several bottleneck problems must be resolved for untapping its potential.

Lignocellulosic biomass is an abundantly available and renewable resource. Because of this, extensive research are ongoing to be able to utilize the biomass as a starting material for the development and synthesis of a wide range of platform chemicals and materials (Beaucamp et al., 2022; Bertella & Luterbacher, 2020; Collins et al., 2019; Mujtaba et al., 2023). Lignocellulosic biomass consists of mainly cellulose, hemicellulose and lignin, which are tightly bonded together. The structural complexity contributes to a high glass transition (T_g) and melting temperature (T_m), in the vicinity of its degradation temperature. This makes the biomass inherently lacking thermoplastic properties. Research efforts are, however, underway to enhance the thermoplastic properties using different approaches, such as various pretreatments and chemical modifications (Abe et al., 2020; Bao et al., 2018; Chen et al., 2017a, 2017b; Feng et al., 2019).

Thermoplasticization of wood via chemical modification has been studied since the 1970s, followed by increased research interest in the following decades (Goldstein, 1975; Kubo et al., 1996; Norimoto et al., 1979; Östberg et al., 1990; Salmén, 1982; Shiraishi et al., 1979; Yoshioka, 1999). At that time, chemical modification with DMF-pyridine and nitrogen tetroxide were used to modify wood materials (Norimoto et al., 1979; Shiraishi et al., 1979). However, the focus was the behavior of the material up to the softening point/second-order transition and not further into the viscous/flow region (Shiraishi, 1993; Shiraishi et al., 1979). The idea of altering wood properties by using plasticizer and introducing thermal flowability was later pursued by Shiraishi (Shiraishi, 1993). However, most of the studies were aimed at introducing thermoplasticity in a single lignocellulose component, and the thermoplasticization of the entire lignocellulose biomass has only been considered recently.

The chemical modification introduces new functional groups on hydroxyl, carboxylic/carbonyl and methoxy sites in the lignocellulosic biomass, which enhances the flowability and thermoplasticity (Bertella & Luterbacher, 2020; Feng et al., 2019; Guo et al., 2018; Li et al., 2021b, a, 2022; Zhao et al., 2016). However, the availability of solvents that rapidly and comprehensively wet and dissolve the biomass are critical for obtaining efficient chemical modification. Moreover, lignin has a tendency of forming C—C bonds due to repolymerization with itself after depolymerization, which inhibits further functionalization (Bertella & Luterbacher, 2020; Zarna et al., 2021; Zhao et al., 2016). This complicates the possibility of enhancing thermoplastic properties in the pristine lignocellulose biomass with all components present. However, with effective solvents, and by controlling the repolymerization process, the possibility of functionalization and introduction of thermoplastic properties increases.

Ionic liquids (ILs) are effective in wetting and dissolving lignocellulosic biomass, hence, making the functional groups available for reactions. Thermoplastic lignocellulose have been produced from mulberry wood via heterogeneous esterification for 2 h in dimethylsulfoxide (DMSO) and 1-butyl-3-methylimidazolium chloride (BMIMCl) with molar ratio of 5.9:1 (DMSO:BMIMCl) (Chen et al., 2017a). However, the high cost of ILs, high boiling point and large amount of solvent requirement for chemical modification of the biomass as well as lack of good flowability, poor mechanical properties, and partial biodegradability of the synthesized thermoplastic lignocellulose materials, raises questions about the eco-friendliness and competitiveness of these processes (Chen et al., 2017a; Sun et al., 2011; Xie et al., 2007). The abundant availability and inexpensiveness of the lignocellulosic biomass, as well as applying the concept of biorefinery, may offset the cost associated with the solvent but the quality and performance of the thermoplastic lignocellulose matters when dealing with feasibility and sustainability of the process and product.

The incentive of substituting fossil-fuel based products with bio-based products have recently gained a strong momentum due to the EU 2050 carbon neutrality strategy and the UN sustainable development goals. Hence, the purpose of this review article is to provide a review on the state-of-the-art of thermoplastic materials developed from the entire

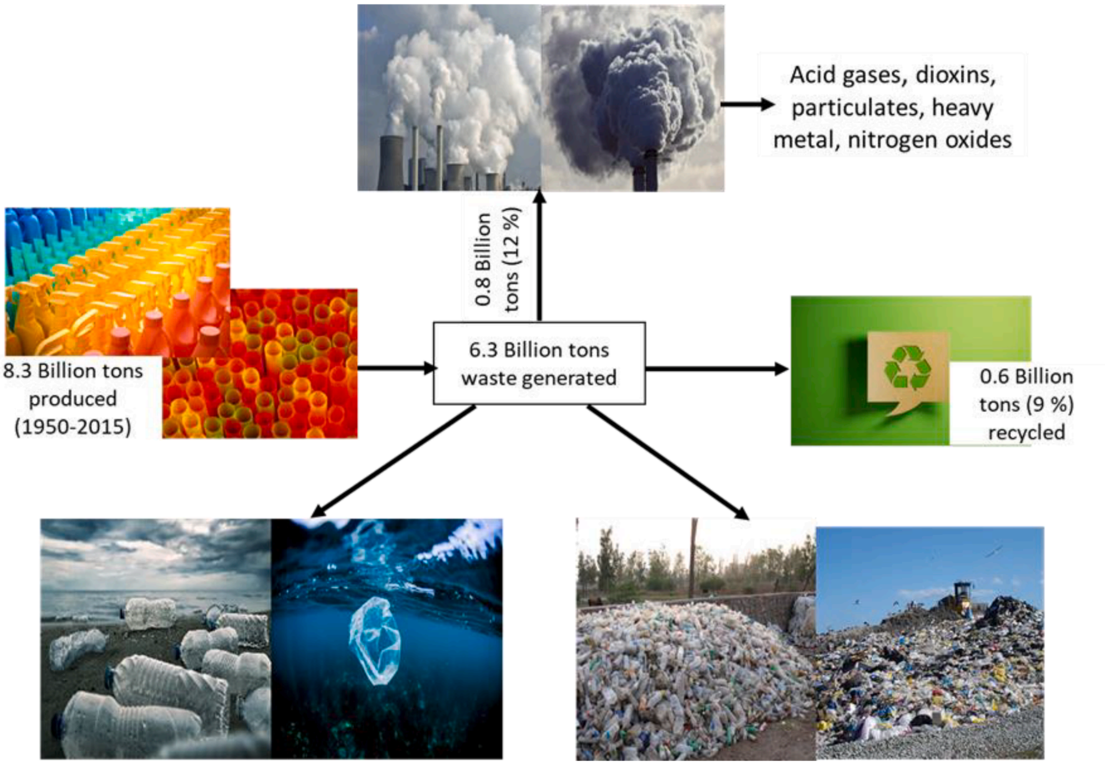

Fig. 1. Illustrations of trends of fossil-based plastic production (from 1950 to 2015) and associated waste generation and potential environmental impact (data obtained from Geyer et al., (2017).

lignocellulosic biomass. Special emphasis is given to the specific modifications and the properties of modified lignocellulose materials (thermal, mechanical, rheological, and chemical properties). Factors affecting the development of thermoplastic lignocellulose and related regulatory and policy issues are also discussed. It also provides information on the challenges and future prospect of producing thermoplastic lignocellulose plastics. The review does not focus on wood plastic composite (WPC) materials, i.e., where the lignocellulose biomass is mixed into a matrix of most often a fossil-based plastic. Materials developed from the major separate components of lignocellulose (cellulose, hemicellulose and lignin), rather than the whole lignocellulose, is not considered here either.

2. Advances towards thermoplastic lignocellulose materials

The current production of bio-based thermoplastic materials from lignocellulosic biomass relies either on fractionating individual components such as lignin, hemicellulose, and cellulose, production of composite films and sheets (from the three lignocellulose components) or WPC's. Developing thermoplastic material from the entire components of lignocellulose biomass is a challenging task. However, research is emerging that focuses on producing thermoplastic materials from all-lignocellulose. Thermoplastic films having a relatively high stiffness (a Young's modulus of 0.9–1.6 GPa) have been developed from lignocellulosic wood pulp by using benzethonium chloride (Hyamine) as a functionalizing agent and sulfuric acid as both a catalyst and functionalizing agent in a reactive extrusion process (Li et al., 2021a, 2021b, 2021c). The attachment of benzethonium group via sulfate species to the lignocellulose wood pulp appeared to lead to the increased flowability of the modified lignocellulose (Li et al., 2021c).

In thermoplastic lignocellulose materials, each of the main biomass components (cellulose, hemicellulose and lignin) should contribute positively to the overall material properties. Therefore, new methodologies are required to maximize the roles of all components in the material development. Recently, a new approach was used to develop lignocellulosic composite films by recombining the components of the biomass after deconstruction (depolymerization) of these. This method was shown to impart toughness and strength of the lignocellulosic film. Especially the use of lignin improves the hydrophobicity, air barrier properties, thermal stability to the material. Lignin can also fill the intermolecular space between cellulose and hemi-cellulose molecules.

A lower water absorption has been observed for thermoplastic films prepared from lignocellulose nanofibrils (LCNF) compared to those from cellulose nanofibrils (Horseman et al., 2017). A film having high UV-absorption, strength and antioxidant activity has been developed from the composite materials: bacterial cellulose, lignin and cellulose nanocrystals, in which lignin was used as a filler (Sá et al., 2020). Increased hydrophobicity and thermal stability were observed in lignocellulose films produced from lignocellulose nanofibrils containing 17% lignin Bian et al., (2018). The toughness of cellulose nanofibril films were doubled after addition of colloidal lignin particles (10%), which also provided good UV- and visible light blocking property (Farooq et al., 2019). The presence of colloidal lignin particles improved the water barrier properties (Farooq et al., 2019). The above examples show the possibilities of obtaining composite films using lignocellulose components for different applications.

A film, developed by depolymerization followed by repolymerization of corncob residues, was shown to have good thermal stability, UV-blocking capacity and hydrophobicity along with good water vapor barrier properties when the lignin content was in the range between 4 and 30% (Song et al., 2021). The developed film had a water permeability of $2.17–2.76 \times 10^{-11}$ g cm/(cm^2 s mmHg), a water contact angle of 86 ° and a UV blocking reaching 99% for UVB (290–320 nm) and 98% UVA (320–400 nm) with an optical transparency of 86%, implying its potential application in food packaging and in electronics (Song et al., 2021). The authors claimed no need of additives, however, ways to recover the IL is important to minimize the production cost (Song et al., 2021). These results show the potential of lignocellulose biomass to produce high value bio-based products in various applications such as windshields, food packaging, medical and electronics. The special and versatile functionalities observed (UV blocking, water permeability, antioxidant activity and hydrophobicity) are due to the presence of lignin.

The presence of hemicellulose in the composite films affects the film overall properties. The content of hemicellulose in Eucalyptus sp. cellulose pulp strongly influenced the apparent viscosity of microfibrillated cellulose suspensions (Claro et al., 2019). Formation of large voids and fiber rapture were observed in the microfibrillated cellulose film made by filtration of the suspension containing Eucalyptus sp. cellulose pulp with lower hemicellulose content (3%), which affected negatively the mechanical strength (Claro et al., 2019). The effect of removing hemicellulose on the microstructure and mechanical properties of microfibrillated cellulose films are shown in Figs. 2 and 3. By reducing the hemicellulose content from 11 to 3% decreased the tensile strength from about 80 MPa to 60 MPa and the strain-to-break from 3.5 to 2% (Claro et al., 2019).

Lignocellulose composite films have been developed from rice straws by alkali depolymerization of the rice straw biomass, followed by TEMPO mediated oxidation to produce alkali cellulose nanofibrils and solution casting at 80 °C (Hu et al., 2016). Repolymerizing the isolated hemicellulose, lignin and cellulose nanofibrils with the help of 30% sorbitol as a plasticizer produced flexible lignocellulose composite films (Hu et al., 2016). The authors observed that by adding 20% alkali cellulose nanofibrils the water vapor barrier, the transparency and the mechanical properties were improved compared to cellulose and hemicellulose/lignin film.

The films had a Young's modulus of 475 MPa, a tensile strength of 21.5 MPa (increased by almost 240%) and a strain at break of 20% (increased by 85%) (Hu et al., 2016). In a report by Ma et al. (2022), covalent bonds between alkali lignin, cellulose nanofiber and konjac glucomannan were reconstructed with epichlorohydrin to obtain lignocellulose composite films. Compared to pure cellulose nanofibril (CNF) films, the addition of 10% konjac glucomannan and 10% alkali lignin improved the UV light barrier (from 54 to 69% for UVB and from 33 to 56% for UVA), increased the hydrophobicity (water contact angle increased from 50 to 80°) and enhanced the mechanical properties (tensile strength from 108 to 131 MPa and tensile strain at break from 3 to 8%) (Ma et al., 2022; J. Yu et al., 2019). Moreover, increasing the alkali lignin content to 20% resulted in water contact angle of 110° and 99% blocking of both UVB and UVA (Ma et al., 2022). The improvement is attributed to the capability of alkali lignin and konjac glucomannan to fill the voids in the cellulose network due to their smaller molecular weight (Ma et al., 2022; J. Yu et al., 2019). Hence, the strategy of depolymerization followed by repolymerization of lignocellulose biomass can help to control the morphology at nano scale. This helps to produce bio-based materials with predictable properties and functionalities. Some thermoplastic lignocellulose products are already available on the market and others are in the final phase of validation to enter the market. Table 1 shows some of the thermoplastic lignocellulose products available in the market developed from lignocellulose and/or bio-based substrates. The products are described as thermoplastic, compostable or biodegradable. However, the condition at which they are compostable (for example industrially compostable or house compostable) are not mentioned and needs to be described in detail.

3. Modification approaches: mechanisms of enhancing thermoplasticity in lignocellulose materials

Native lignocellulosic biomass lacks thermoplastic properties, such as moldability and flowability at elevated temperature. There are however several approaches to introduce thermoplasticity in lignocellulosic materials, including chemical modification, ring opening,

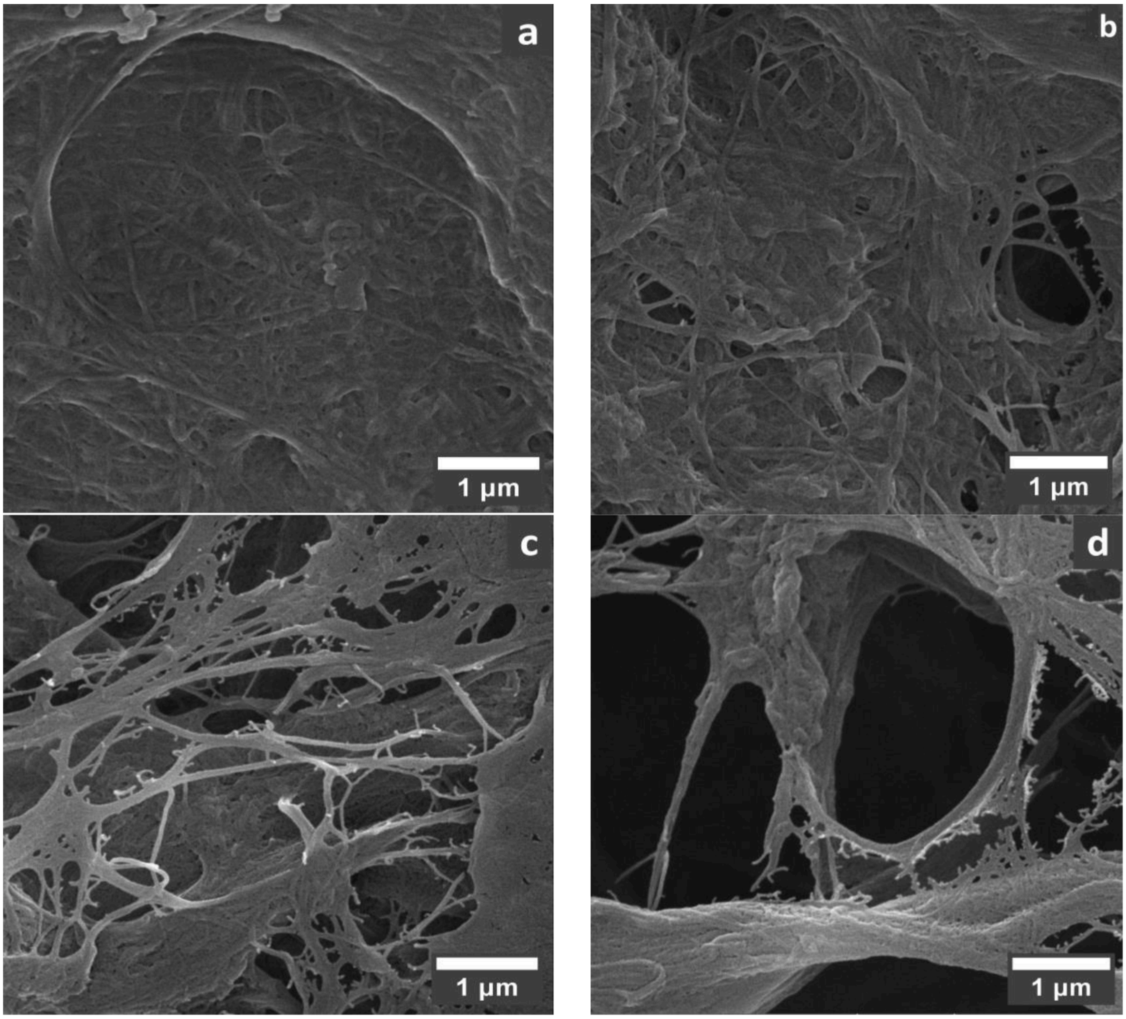

Fig. 2. SEM images of microfibrillated cellulose films showing the relationship between hemicellulose content and void formation (a) 16% hemicellulose (b) 11% hemicellulose (c) 8.3% hemicellulose and (d) 3% hemicellulose. Reproduced with permission from Claro et al. (2019). Copyright 2019 Elsevier.

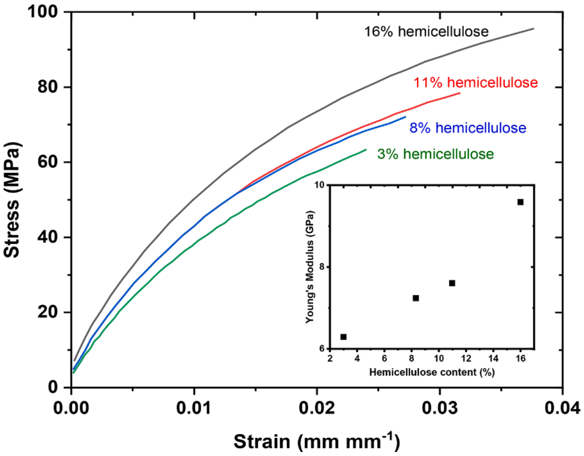

Fig. 3. Mechanical properties of lignocellulose films after removal of hemicellulose. Drawn after (Claro et al., 2019).

fermentation coupled with grinding, reactive extrusion and/or combinations of two or more of these processes. Addition of plasticizers, lower molecular weight species used to make polymers soft and flexible, are the main step in most of the modification processes after swelling and depolymerizing the biomass. Plasticizers enhances the flowability and mechanical flexibility of the material by reducing the polymer intermolecular forces (Donhowe & Fennema, 1993; Marcilla & Beltrán, 2017). The enhancement of thermoplasticity with plasticizers normally occurs at the expense of mechanical strength and stiffness. Hence, ways to avoid critical loss in strength while enhancing flexibility and plasticity are important to explore.

The integration of reactive extrusion and mechanochemistry are gaining attention due to their high efficiency of solvent utilization compared to e.g., esterification, etherification and other chemical modification methods. Even though reactive extrusion is a step towards cheaper processing it is still far from conventional plastics. Therefore, research efforts are required to reduce the price gap. Using solvent recycling and finding ways to enhance thermoplasticity with a minimum number of process steps will contribute to this. The modification approaches commonly used for thermoplastic lignocellulose are described in detail in the following sections. Fig. 4 gives an overview of the different ways of enhancing thermoplasticity in lignocellulosic materials.

3.1. *Chemical modification (esterification, etherification, and benzoylation)*

The structure and properties of lignocellulosic biomass material can be altered by various chemical modification methods via the introduction of different functional groups. The most common chemical

Table 1
Thermoplastic lignocellulose materials/products on the market.

Application	Product type	Raw material	Production method	Company	References, Web address
food packaging	single use bags, cups and bowls	lignin and compostable polymer	extrusion, injection molding and vacuum forming	Cyclewood associates	https://cyclewood.com/ (Cyclewood associates) (Accessed date, 21 Jul 2022)
food containers and packaging	trays, plates, cups and lids, cups and straws	bagasse/sugarcane, bamboo, soft wood, hard wood	molding	Footprint	https://www.footprintus.com/solutions (Footprint) (Accessed date, 14 Jul 2022)
food containers and packaging	bowls, hot, cold cups & lids bags, plates	bamboo and sugarcane bagasse	molding	World Centric	https://www.worldcentric.com (Worldcentric) (Accessed date, 21 Jul 2022)
car interior, music instruments, toys, urns	Pellets	lignin and natural fiber (flax, hemp etc…) + additives	Injection molding and extrusion	Tecnaro Gmbh	https://www.tecnaro.de/en/ (Tecnaro) (Accessed date, 14 Jul 2022)
Packaging, household items, office supply, flexible cards, toys, sport equipment	pellets	PHA, PCL, polyester, starch, PLA, bio-polyolefins (bio-PE), bio-polyamides (bio-PA), lignin, natural resins, cellulose, natural waxes, natural oils, & additives	blow molding, extrusion, 3d printing, melt spinning & thermoforming	Tecnaro Gmbh	https://www.tecnaro.de/en/ (Tecnaro) (Accessed date, 14 Jul 2022)
food containers and packaging	plates, cups, spoons, bowls, & drinking straws	birch tree, bamboo, cardboard, palm leaf, wheat straw	molding	Greenlid	https://www.mygreenlid.com (Greenlid, 2022) (Accessed date, 14 Jul 2022)
food services	forks spoons knives	birchwood	–	Eco-woodpro	https://eco-woodpro.com/production (Ecowoodpro 2022) (Accessed date, 21 Jul 2022)
food containers and packaging	plates cutlery take-away boxes, bowls and bags	Birchwood, sugarcane fiber, PLA,	–	Biopak	https://se.dunigroup.com/en/biopak (Biopak, 2022) (Accessed date, 21 Jul 2022)
containers for holding liquid materials	bottle	old corrugated cardboard boxes, and newspapers + plastic (inner liners)	molding	Ecologic brands	https://www.ecologicbrands.com (Ecologic powered by jabil) (Accessed date, 14 Jul 2022)
coffee container (cold)	coffee cups forks spoons	pine and birchwood	–	Biofutura b.v.	https://www.biofutura.com/en/ (Biofutura, 2022) (Accessed date, 21 Jul 2022)

modification methods used for introducing thermoplasticity in lignocellulosic biomass are esterification, acetylation, sulfonation, benzoylation, nitration, sulfomethylation, etherification, amination, and halogenation. Chemical modification processes involve mainly the replacement of hydroxyl groups (OH) with other functional groups and spacers (Abe et al., 2020; Bao et al., 2018; J. Chen et al., 2017a; M. J. Chen & Shi, 2015; Guo et al., 2018; J. Li et al., 2021a; Suzuki et al., 2021a). The modification can also target methoxy and carbonyl groups on the lignocellulosic chains (Bertella & Luterbacher, 2020; Zarna et al., 2021; Zhao et al., 2016). The reactions between the hydroxyl, carbonyl, methoxy and functionalizing agents are often initiated with the aid of a catalyst. The reaction introduces new properties such as flowability, flexibility, and moldability to the material by interfering with the functional groups and hydrogen bonds within the lignocellulose biomass components (J. Chen et al., 2017a, 2017b M. J. Chen & Shi, 2015; Feng et al., 2019; Guo et al., 2018; J. Li et al., 2021a; Suzuki et al., 2021a). The effects on the thermoplasticity depend on the reaction conditions, reactive components and the type of biomass used. The chemical modification involves the acetyl group (-$COCH_3$), sulfate group (-SO_3), nitrate group (-NO_3), amine (-NH_2), which are reacting with hydroxy, methoxy and carbonyl sites on hemicellulose, cellulose and lignin. Proposed chemical modification mechanism of thermoplastic lignocellulose material development from the three major lignocellulose components (considering acetylation) is shown in Fig. 5.

ILs and deep eutectic solvents (DES) are commonly used as solvents in the modification process. E.g. thermoplastic films have been prepared by homogenous modifications of sugarcane bagasse in 1-allyl-3-methylimidazolium chloride (AMIMCl) with phthalic anhydride (PA) (Chen & Shi, 2015). The NMR signals at 169.63 ppm (carbon originating from the acetyl group of hemicellulose), 168.55 ppm (carbon in the aromatic carboxyl group) and 168.03 ppm (carbon in aromatic ester) indicated that the chemical modification occurred in all the three components (cellulose, hemicellulose and lignin) via ester bonds (M. J. Chen & Shi, 2015). A decrease in the IR absorption intensity of the O—H bond at 3420 cm^{-2} and the shift of the peak at 1735 down to 1718 cm^{-1} further confirm the formation of ester bonds between the three major components of sugarcane bagasse and the phthalic group (Chen & Shi, 2015). The NMR data further shows that the phthalic groups are partially attached at the hydroxyl group positions on the C2, C3 and C6 positions on the polysaccharides (Chen & Shi, 2015). In the modification process the PA act as internal spacer/plasticizer and introduce thermoplasticity (T_g ranges between 133 and 175 °C and elongation at break is almost 22%). The tensile strength is reduced from 30 to 3.5 MPa mainly due to partial hydroxyl substitution, spacer effect, but also due to some degradation during the modification process (Chen & Shi, 2015). Thermoplasticity was enhanced in Eucalyptus biomass material in a two-step process using continuous steam explosion followed by an oxidation–reduction process (Feng et al., 2019). The amount of cellulose, hemicellulose and lignin fractionated during the steam explosion process, the reaction mechanism involved and the effect of lignin on the overall modification process were not explored (Feng et al., 2019). The modification of sugarcane bagasse in an IL-based transesterification process (20% hexanoyl and 80% long chain acyl groups, vinyl decanoate) yielded a thermoplastic film with good thermal and mechanical properties (a tensile strength of 35 MPa and melt flowability at 180 °C) (Suzuki et al., 2021). The substitution of all hydroxyl groups and retaining the hemicellulose and lignin in the bagasse maintained the mechanical properties (Suzuki et al., 2021). Further work is, however, needed to determine fully the reaction mechanisms in the entire lignocellulose material and the effects of lignin and hemicellulose on the melt flowability and overall thermoplasticity, which is important to design mechanically flexible thermoplastic lignocellulose material.

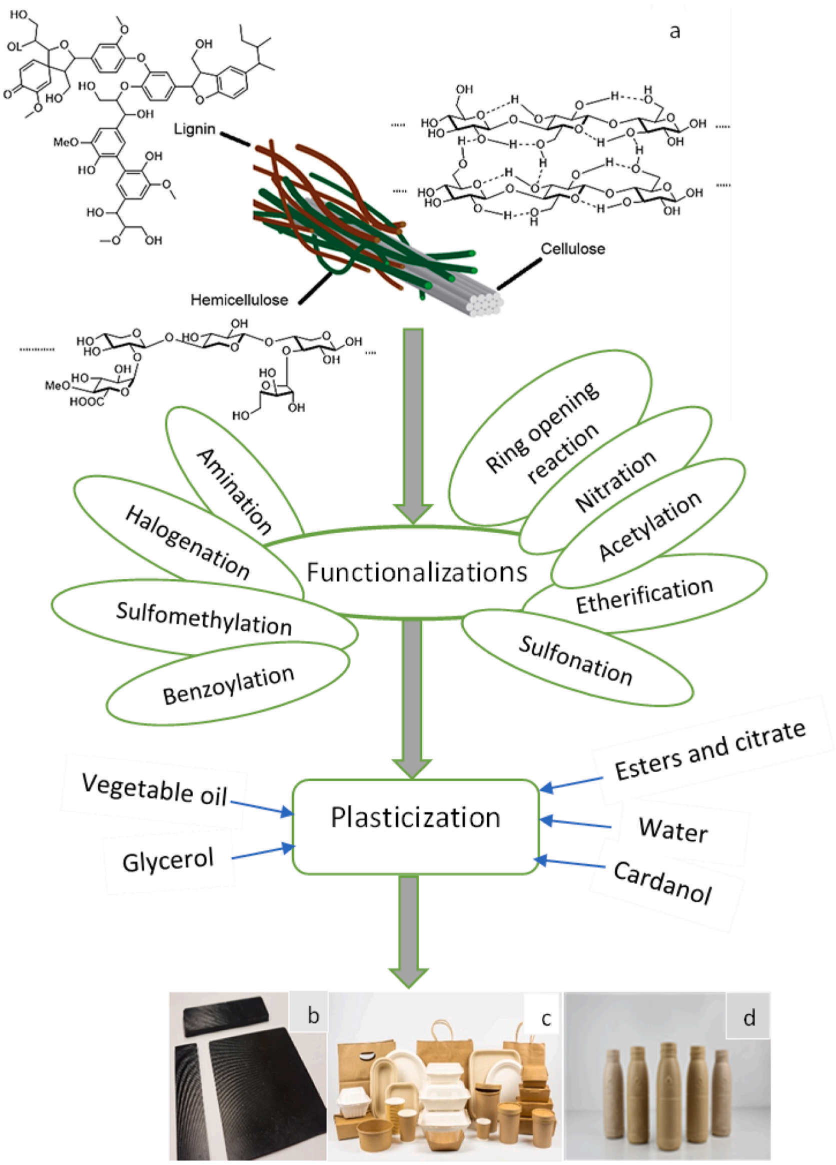

Fig. 4. a) Schematic illustration of the three major components of lignocellulose (Li & Takkellapati, 2018) and typical modification methods to enhance thermoplasticity, Reproduced with permission from John Wiley and Sons. Copyright 2018 Society of Chemical Industry and John Wiley and Sons, Ltd. b) Image of compression molded lignocellulose (see Fig. 12 for details) (J. Li et al., 2021a). Reproduced with permission from Elsevier. Copyright 2021 Elsevier c) Image of different lignocellulose-based molded items and paper bags (BIM kemi 2022). Reproduced with permission from BIM kemi, Copyright BIM kemi 2022 d) Lignocellulose-based bottles (PulPac 2022). Reproduced with permission from PulPac Copyright (PulPac 2022).

Even though chemical modification imparts good thermoplastic properties, several factors hinder its application for upscaling. The main challenges are the requirement of large quantities of solvents, inadequacy of dissolving the entire biomass and the long reaction times. Further the repolymerization of lignin and side reactions, such as crosslinking of aldehyde and unreacted hydroxyl group after periodate oxidation need to be controlled and minimized, for example, periodate oxidation followed by reduction (Bertella & Luterbacher, 2020; Codou et al., 2015; Willberg-keyrila et al., 2017; Zarna et al., 2021; Zhao et al., 2016). The above issues contribute to an increasing overall production cost of the modified lignocellulosic materials (Bertella & Luterbacher, 2020; Codou et al., 2015; Willberg-keyrila et al., 2017; Zarna et al., 2021; Zhao et al., 2016). To overcome these problems, chemical modification assisted by mechanochemistry such as reactive extrusions are seen as potential alternatives for modifying the biomass and improving the thermoplastic properties of modified lignocellulosic materials.

3.2. *Mechanochemistry assisted/coupled with chemical modification*

Mechanochemistry is defined as “chemical reaction that is induced by the direct absorption of mechanical energy” (Horie et al., 2004). The mechanical energy can be introduced in a variety of ways, such as grinding, mechanical shearing, compression, stretching and impact, which activates chemical reactions by creating more active sites, macroradicals and by reducing the particle sizes (Horie et al., 2004). Mechanochemistry-assisted chemical reactions can significantly reduce the amount of solvent needed and increase the reaction kinetics (Darwish et al., 2019; Howard et al., 2018). The reduction in particle sizes and transformation of cellulose into more amorphous forms are observed when exposing lignocellulose biomass to “mechanochemical” treatment (Pérez-Merchán et al., 2022).

Defibrillation by milling / grinding and subsequent reactive extrusion is used as a tool for developing thermoplastic lignocellulose. These processes create a larger access to the lignocellulose functional groups, making the reaction more effective and efficient. Mechano-catalytic esterification of sugarcane bagasse by ball milling resulted in modified bagasse with high thermal stability and degree of acetylation (Zhang et al., 2018). The action of ball milling and pyridine destroyed the crystalline structure and created a way for the acetylation agent to reach further into the bulk of sugarcane bagasse (Zhang et al., 2018). Thermoplastic lignocellulose with good thermal stability and mechanical properties have been produced by mechanochemistry. However, a precise temperature control during milling is difficult to achieve due to local heat generation induced by the mechanical impact. Moreover, the

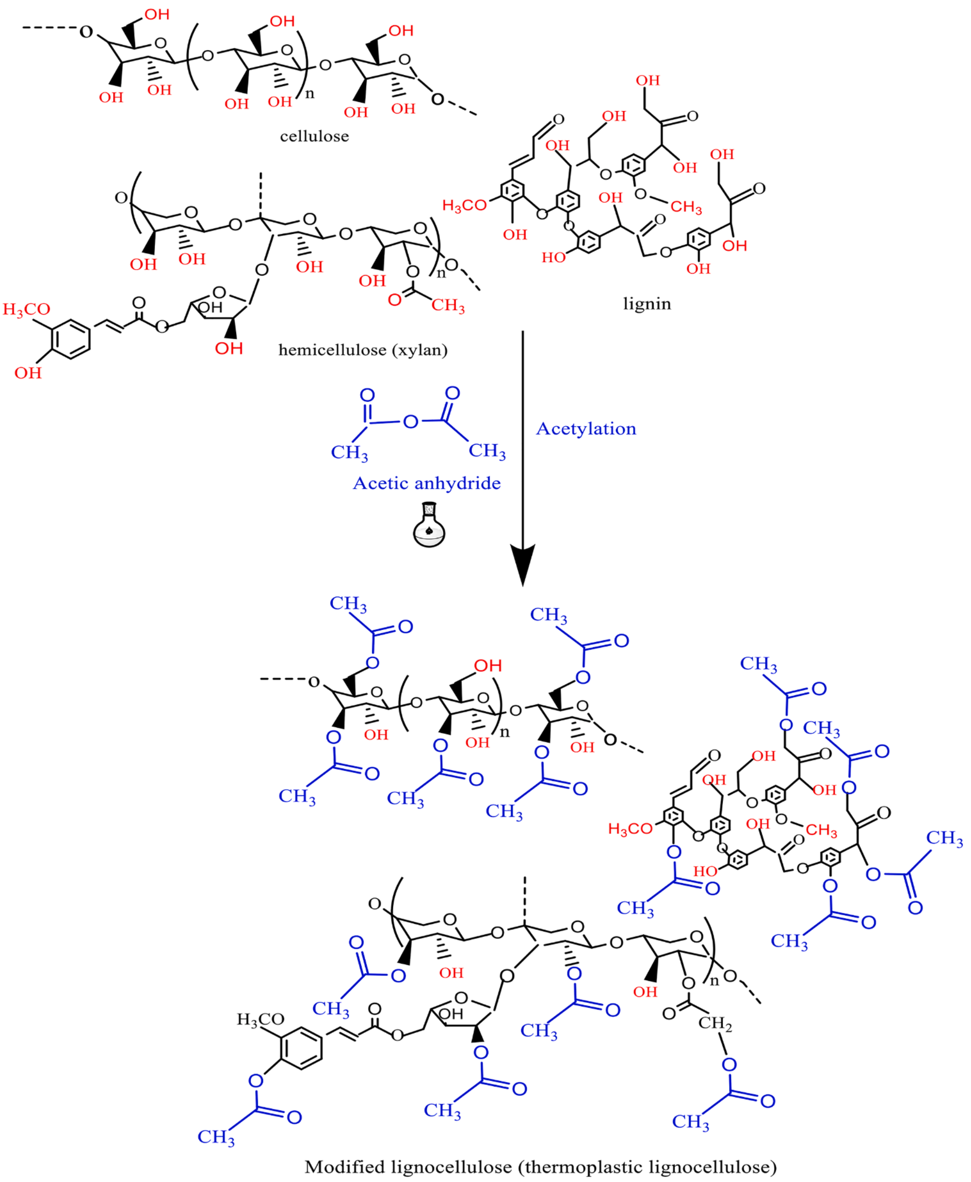

Fig. 5. Proposed reaction routes for thermoplastic lignocellulose development, assuming partial substitution of hydroxyl and methoxy groups: the case is for acetylation. Note that the chemical structures illustrated are only examples.

milling process is relatively energy intensive compared to twin screw extrusion (Espinosa et al., 2019; Rol et al., 2017). This makes the overall milling process less favorable than extrusion for thermoplastic lignocellulose development.

A thermoplastic lignocellulose material was developed directly through acetylation in alkali assisted extrusion of Eucalypt powder, which led to enhanced mechanical and thermal properties (Tian et al., 2022). The T_g of the produced material, having a high degree of acetylation (52%), was 135 °C, which is lower than the T_g of pure cellulose acetate, most likely due to that the modification occurred in the lignin component of the material. Thermoplasticity was achieved through the synergetic effects of NaOH treatment and extrusion of the resulting swollen biomass. This transformed the more crystalline cellulose I to the more reactive and less crystalline cellulose II, making the biomass readily accessible for acetylation (Tian et al., 2022).

The reactive extrusion process is seen as a potential way of imparting thermoplasticity in the entirety of the lignocellulosic biomass, without the need of removing any of its components. However, for a fully successful process, the effects of lignin and hemicellulose and their reaction mechanisms still need to be further explored. The main challenge with the reactive extrusion technology is to match the short reaction time with the rate of the chemical reactions to achieve the desired degree of modifications. Thus, ways to overcome this challenge should have to be devised to harness the full potential of the reactive extrusion process for developing thermoplastic lignocellulose materials. The impact of lignocellulose modification on thermoplastic properties are shown in Table 2.

3.3. Ring opening reactions

The molecular structure of lignocellulosic materials can through ring opening processes be altered and thus yield materials with new functionalities and properties. Polysaccharides (cellulose and hemicellulose) are modified by these mechanisms through selective breaking of the C2-C3 bonds in the glucose repeating unit (Börjesson et al., 2019; Larsson & Wågberg, 2016; Palasingh et al., 2022; Stenstad et al., 2008). The chemically modified material shows great potential in a variety of applications. Further developed dialcohol cellulose material from bleached softwood kraft fiber with improved thermoplastic and mechanical properties (strain at break of 44% and tensile strength of 57 MPa), was

Table 2
Modification routes of lignocellulose to achieve thermoplasticity.

Biomass type	Types of modification	Processing methods	Improved Properties	Challenges	References
Eucalypt wood	Acetylation	Extrusion	Relatively high window of processing temperature, 70–80 °C	High solvent requirement	(Tian et al., 2022)
Mulberry wood	Glycerol and glycerol triacetate	Extrusion and injection molding	T_g introduced	Irritating gas formation in extruder, above 170 °C	(Li et al., 2022)
Spruce wood	Esterification	Hot pressing	Hydrophobicity, translucent film and window of processing temperature, 120–200 °C	Degradation at higher temperature (200 °C)	(Sejati, Akong, & Torloting, 2022)
Aspen pulp (8.2% lignin)	Acetylation and reuse of extrudates (recycle stream)	Extrusion	Flowability and melt moldability, high stiffness	Degradation at higher liquid modifier concentration	(Li et al., 2021b)
Aspen pulp (8.2% lignin)	Butylation	Reactive extrusion	Moldable and flowable, high stiffness	Formation of black color, higher rate of degradation during molding	(J. Li et al., 2021a)
Wood residues	Grafting of n-octanol	Chemical modification	Hydrophobicity, excellent flexibility and processability, wide range in processing temperature (80–240 °C)	The reaction takes place with the presence of nitrogen, which might increase the cost and create scale up issues	(Bao et al., 2018)
Mulberry wood	Acetylation	Injection molding and film making	Translucent appearance	Thermal stability reduced, lower window of processing, significant decomposition of components	(J. Chen et al., 2017a)
Sugarcane bagasse	Transesterification	Solution casting	Flexible film (stretchability, tensile strain increased from 4 to 59%), and good UV blocking ability	High solvent requirement, significant decrease in tensile strength	(J. Chen et al., 2017b)
Sugarcane bagasse	Chemical modification with phthalates in IL	Solution casting	Flexible film (stretchability, tensile strain increased from 3 to 22%)	Use of petroleum-based plasticizer, phthalates, Long reaction time, lower tensile strength	(M. J. Chen & Shi, 2015)
Mulberry wood	Ball milling and mixing in IL	Kneading	Flowability	Use of IL as a solvent expensive	(J. Chen et al., 2015)

obtained by compression molding at 150 °C (Larsson & Wågberg, 2016). Mechanical properties of modified cellulose fibers were observed to depend on the types of functional groups introduced (López Durán et al., 2018). It was found that relatively ductile fibers could be obtained by sequential treatment with periodate oxidation followed by borohydride reduction. The material had a strain at break of 15% and a strength at break of 175 MPa (López Durán et al., 2018).

The T_g of homogeneously modified fibers (yielding dialcohol cellulose) was found to decrease with increasing level of oxidation, the T_g decreased from 160 to 75 °C as the oxidation level increased from 24 to 91%, indicating improved processability of the modified product (Kasai et al., 2014). The mechanism of chemical modification of cellulose fibers to introduce new functional groups via periodate oxidation, TEMPO oxidation, sodium borohydride reduction and combinations of these are described in detail in Table 3 and Fig. 6 (López Durán et al., 2018).

3.4. Monomers and polymers from lignocellulose biomass

The fractionation of lignocellulose biomass through chemical treatment produces furfural and 5-hydroxymethylfurfural (HMF), which are precursor chemicals for many products and HMF is known as ‘‘the sleeping giant’’ of sustainable chemistry (Deng et al., 2022; Galkin & Ananikov, 2019). Oxidation of HMF produces 2,5-diformylfuran (DFF), formyl 2-furancarboxylic acid (FFCA), furan-2,5-dimethylcarboxylate (FDMC), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) and 2,5-furandicarboxylic acid (FDCA). FDCA is a monomer that can be used to produce poly(ethylene furanoate) (PEF) and the other chemicals are used as intermediates in pharmaceuticals and furan-based polymer development (Deng et al., 2022; Liu et al., 2022). Furan-based chemicals are also produced via biotechnological methods by employing whole cells or enzymes (Lalanne et al., 2021). PEF is biodegradable and has great potential to replace poly(ethylene terephthalate) (PET), however, the synthesis of PEF via conventional polycondensation is still challenging due to its thermal degradation and undesirable color formation during the long reaction time, days (Knoop et al., 2013; Pellis et al., 2016; Rosenboom et al., 2016, 2018; Terzopoulou et al., 2017). Recent works on ring opening polymerization has, however, shortened the reaction time (Carlos Morales-Huerta et al., 2016; Pfister et al., 2015; Rosenboom et al., 2018). PEF with more than 95% conversion and a molecular weight above 30 kg/mol has been obtained by ring opening polymerization of methyl FDCA and ethylene glycol in less than 30 min Rosenboom et al. (2018). HMF is indeed emerging as a building block for sustainable platform chemical production, however, conversion efficiency and production cost are remaining challenges for industrial scale production (Birmingham et al., 2021).

Table 3
Description of chemical modifications shown in Fig. 6. Reprinted with permission from López Durán et al., (2018). Copyright 2018 American Chemical Society.

Chemicals used in the modification	Reaction condition
(1)	Starting material (cellulose)
(2) $NaI0_4$	Periodate oxidation for 2 h at 50 °C
(3) $NaI0_4$:$NaBH_4$	Periodate oxidation for 2 h at 50 °C followed by reduction by sodium borohydride during 2 h at room temperature
(4) $NaI0_4$ + NH_2OH/$NaBH_4$	Periodate oxidation during 2 h at 50 °C, reductive amination for 2 h at room temperature with hydroxylamine hydrochloride, and in-situ reduction with sodium borohydride for 2 h at room temperature
(5) $NaI0_4$ + $NaClO_2$	Periodate oxidation during 2 h at 50 °C and chlorite oxidation for 48 h at room temperature
(6) TEMPO	TEMPO oxidation for 48 h at 40 °C
(7) TEMPO + $NaI0_4$	TEMPO oxidation during 48 h at 40 °C and Periodate oxidation for 2 h 30 min at 50 °C
(8) TEMPO + $NaI0_4$ + $NaBH_4$	TEMPO oxidation for 48 h at 40 °C, Periodate oxidation during 2 h 30 min at 50 °C and reduction with sodium borohydride for 2 h at room temperature
(9) TEMPO + $NaI0_4$ + $NaClO_2$	TEMPO oxidation for 48 h at 40 °C, Periodate oxidation during 2 h 30 min at 50 °C and chlorite oxidation for 48 h

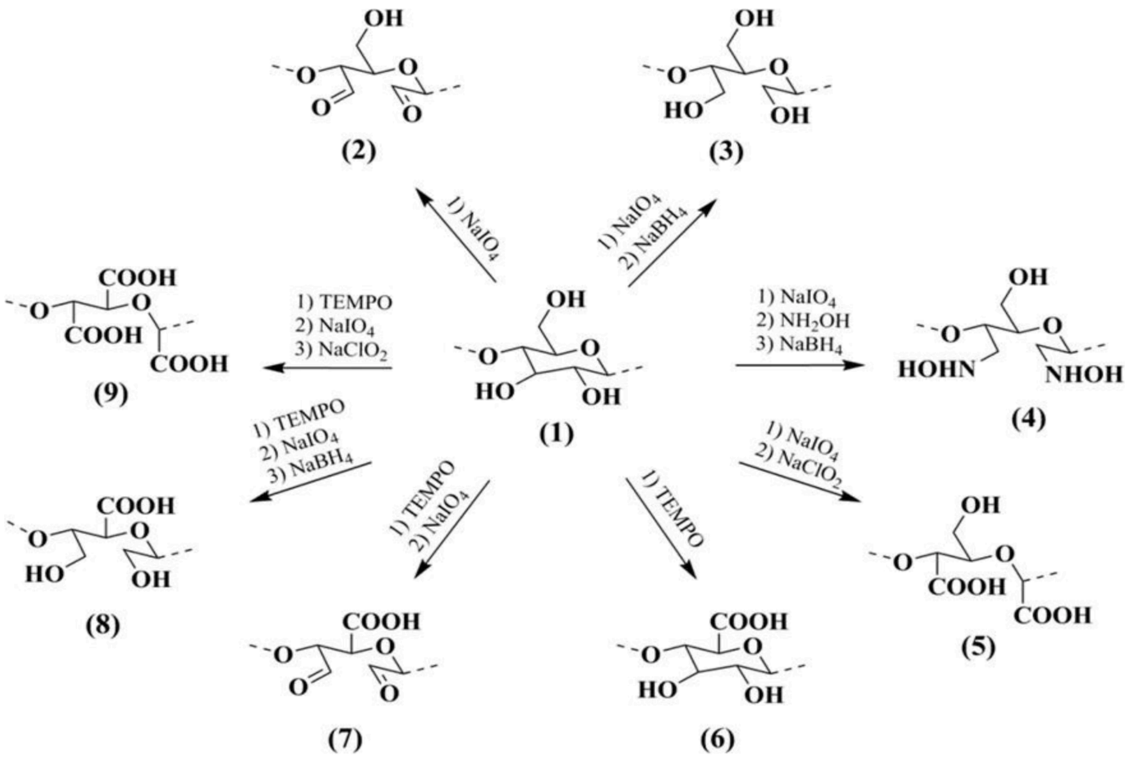

Fig. 6. Illustrations of chemical modification of cellulose fibers by ring opening reaction (López Durán et al., 2018). Reproduced with permission from American Chemical society. Copyright 2018 American Chemical society.

4. Properties of thermoplastic lignocellulose materials (modified lignocellulose)

The overall properties of thermoplastic lignocellulose materials are mainly dependent on their molecular structures and compositions of the biomass, which ultimately determines whether the material complies with the intended purpose or not. Mechanical, rheological and thermal properties can be altered by various modification approaches and these properties are described below.

4.1. *Mechanical properties*

Various approaches are used to enhance the physicochemical properties of lignocellulose based materials (discussed above in the section on modification approaches). It is important that the desired physicochemical properties of thermoplastic lignocellulose are transferred to the new material, such as ductility and the preservation of as much natural strength as possible. As mentioned earlier, Tian et al. (2022) developed a thermoplastic lignocellulose material with moldability in compression molding, using alkali extrusion and acetylation (Tian et al., 2022). The lignin component was retained, and a highly acetylated thermoplastic material were developed after depolymerizing the Eucalypt powder by alkali treatment and functionalization with acetic anhydride (Tian et al., 2022). However, the product is quite brittle and it was difficult to measure the toughness, elongation and tensile strength due to the short chains of alkanoates formed and introduced during acetylation (Tian et al., 2022). Li et al. (2021) also observed low tensile strain, less than 1%, and a low tensile strength of modified lignocellulose material (J. Li et al., 2021a). On the other hand, the mechanical strength of modified mulberry powder was improved from 13 to 26.6 MPa after plasticizing it with 14% glycerol and glycerol triacetate, respectively, by dissolving the mulberry powder in 3% NaOH and 7% urea at –10 °C (Li et al., 2022; Yu et al., 2018). The processability of the modified lignocellulose depends on the flow properties introduced during modification, extrusion and injection molding processing techniques. In most cases, the improved flowability and melt properties are achieved at the expense of tensile strength. Hence, during development of thermoplastic lignocellulose, optimization on how to retain the natural mechanical properties upon introduction of thermoplasticity needs to be considered.

4.2. *Thermal properties*

Thermoplastic lignocellulose exhibits 3 regions of mass loss in a pyrolysis (nitrogen atmosphere) thermogravimetry experiment: i) the first mass loss below 200 °C is attributed to the evaporation of water and possibly other volatile components, ii) the second mass loss region is attributed to the degradation of hemicellulose and amorphous cellulose (between 180 and 250 °C), as well as of crystalline cellulose from around 240 °C to around 360 °C, and iii) lignin degradation that occurs roughly between 360 and 540 °C (Li et al., 2022; Peredo et al., 2016; Soto-Salcido et al., 2020). The substitution of hydroxyl groups with PA species reduces the onset of degradation from 250 to 175 °C, which is attributed to the hydrogen bond rapture (M. J. Chen & Shi, 2015).

The thermal stability of modified mulberry biomass was decreased due to plasticization with glycerol in the presence of NaOH/urea (Li et al., 2022; Yu et al., 2018). The same trend was observed for modified mulberry, using PA as a modifier/plasticizer provided through an ionic liquid solvent (Su et al., 2015). However, the use of PA is of increasing concern due to its potential health risk, and it is generally recommended to avoid it in production. The thermal stability in inert atmosphere of modified Eucalyptus was improved by 5 °C, from 377 °C to 383 °C, and the melt processing window (the size of the temperature range between T_g and the onset of degradation) increased by roughly 75 °C after acetylation (Tian et al., 2022). A broader processing temperature range is preferable since it allows for an optimization of properties in a variety of different applications. It also often makes the processing easier (more heat-tolerant material).

The T_m and T_g are important thermal parameters, which determine both the processing conditions and the final applications. T_g of 135 °C for acetylated Eucalyptus material and 164 °C for lignocellulosic pulp material, containing 8.2% lignin, has been reported (Li et al., 2021b; Tian et al., 2022). Yet, the acetylation of the Eucalyptus biomass after alkali pretreatment, produced a material with poor moldability (Tian et al., 2022). However, acetylation of lignocellulose biomass in the presence of benzethonium chloride and sulfuric acid as functionalizing agent and catalyst yielded, as mentioned earlier, a modified lignocellulose with good flowability, which was possible to compression mold (J. Li et al., 2021a). This was attributed to the attachment of benzethonium sulfate on the lignocellulose material (J. Li et al., 2021a). Formation of hydrogen bond by the attachment of glycerol and/ free amide group from urea to the hydroxyl groups of cellulose in mulberry powder, extruded in the presence of a NaOH/urea solution, yielded thermoplastic lignocellulose with a T_g at 97 °C (Li et al., 2022; Yu et al., 2018). The T_g is far lower than the decomposition temperature indicating the melt processability and thermoplasticity of this modified biomass material. The extrusion conditions for producing the modified wood materials were at a temperature of 155 °C and a screw speed of 60 rpm (Li et al., 2022). Evaporation of the plasticizer and decomposition of the wood material was observed if the extrusion temperature exceeds 155 °C (Li et al., 2022). Benzylation of wheat straw and mulberry branches in a NaOH treatment improved the thermoplasticity of the lignocellulose material (J. Chen et al., 2014). The modified biomass showed good melt processability at 140 °C and 180 °C in extrusion and injection molding, respectively (J. Chen et al., 2014). Modification with two different ratios of PA and sugarcane bagasse (2:1 to 5:1) reduced the T_g of the material from 175 to 133 °C (M. J. Chen & Shi, 2015). It is possible to conclude that the overall thermal properties of thermoplastic lignocellulose are highly dependent on the processing conditions, types of plasticizers and modifiers used and to some extent type of biomass. Table 4 shows detailed descriptions of processing conditions and properties of thermoplastic lignocellulose materials.

4.3. Rheological properties

Understanding the viscoelastic properties of modified lignocellulosic biomass is important to be able to optimize the processability and choose process type. This knowledge helps to reduce or avoid the risk of flow abnormalities. The use of rheological tests to mimic the performance of a material during processing at an early developing stage minimizes the risk of ending up with a material with poor processability. Parameters, such as storage modulus (G'), loss modulus (G''), damping and complex viscosity, are determined from the rheology test and are used for the assessment of the processing properties. G' shows the elastic nature of the material, and G'' shows the viscous nature, over a given frequency range, temperature and applied stress/strain.

The thermoplasticity, such as flowability and melt processibility, is determined from rheological measurements, which is used to assess the processability of a new material in conventional plastic processing equipment (e.g. in extrusion and injection molding). Fig. 7 shows the temperature dependence and effects of different T_g's on the melt viscosity of modified lignocellulose material (J. Li et al., 2021a). A T_g of 77 – 87 °C were obtained for the lignocellulose material modified with butyric anhydride, whereas a T_g of 123 and 153 °C was obtained for the acetic anhydride modified lignocellulose (J. Li et al., 2021a). The shear viscosity of all the modified lignocellulose materials decreased with increasing temperature above T_g, to the extent that they showed some sort of thermoplasticity (J. Li et al., 2021a).

The lignocellulosic pulp modified with butyric anhydride showed the most liquid/melt-like behavior below 150 °C (Li et al., 2021b). This indicates, as also shown by T_g, that butyryl groups contribute more to the molecular mobility than acetyl groups (J. Li et al., 2021a). However, the acetylated lignocellulose showed a pronounced decrease in viscosity at temperature above 160 °C, when reactive extrusion with a recycled lignocellulose stream was used (Li et al., 2021b). To put these data in perspective, a PLA material was also included in the plot (Fig. 7). Although several parameters affect the rheological behavior, such as molar mass and molar mass distribution, it is clear that these lignocellulose materials are less thermoplastic (more solid like) than the specific relatively high-viscous polymer (PLA).

The viscosity as a function of shear rate of the acetylated lignocellulose (processed differently and with more liquid modifiers) is plotted in Fig. 8, together with a low density polyethylene (LDPE) and a wood plastic composite (WPC, with polypropylene as the matrix). The shear viscosity of acetylated lignocellulose drastically decreases as shear rate increases, showing strong shear thinning behavior (Li et al., 2021b). The flow behavior observed is comparable to those of rosin and polyethene wax (Li et al., 2021b) indicating that the processability of the modified lignocellulose is sufficient for extrusion. Compared to the LDPE, the thermoplastic lignocellulose showed stronger shear thinning behavior while the wood plastic composite and LDPE showed similar shear thinning behavior in the higher shear rate region.

Thermoplastic lignocellulose with a melt temperature of 182 °C was developed by acetylation of sugarcane bagasse in the presence of an ionic liquid solvent (Suzuki et al., 2021, 2021). The transition from solid-like to liquid-like viscosity behavior, along with a decrease in G', and related changes in G'', are obviously important to assess the stability

Table 4
Thermoplastic lignocellulose processing conditions and technology levels of specific lignocellulose materials.

Raw materials	Processing Method	Processing conditions	Product properties				TRL	References
			TS[a], (MPa)	EB[b], %	T_g, (°C)	T_m, (°C)		
Eucalypt wood	alkali extrusion	10% NaOH, 80 °C, 80 rpm, 1:6 solid to liquid ratio	–	–	135	160	3	(Tian et al., 2022)
Mulberry branches	extrusion and injection molding	Ball milled mulberry to NaOH/urea of 1:5 for 1 h @ −10 °C + 4 h 20 °C, 0.5 h, 14% glycerol, 60 rpm, 120 °C	26.6	3.9	93	155	3	(Li et al., 2022)
Aspen pulp (8.2% lignin)	reactive extrusion	120 °C, 100 rpm, 0.5 kg/h, 13:1:0.95 (CH_3COOH, Hyamine, H_2SO_4)	24	4.3	114–126	–	4	(Li et al., 2021b)
Wood pulp	reactive extrusion	1.2H_2SO_4/Hyamine, 120 or 140 °C, 0.5 kg/h, 100 or 300 rpm	23–32 (FS)	–	72–80	–	4	(J. Li et al., 2021a)
Mulberry wood	extrusion & injection	2 h reaction time, DMSO:BMIBMCl, 5.9:1 and 155 °C, 50 rpm & 155 °C, 550 bar	25	–		155	3	(J. Chen et al., 2017a)
Wood residues	grafting of n-octanol	IPDI & DMAc, 1:1, 1 h, Octanol added at 60 °C, 2 h			54		3	(Bao et al., 2018)
Sugarcane bagasse	solution casting	5 h mixing 0.5 g bagasse in 19.5 g EmimAC at 110 °C Venyl ester added 70 °C	36	4	158	–	3	(J. Chen et al., 2017b)
Sugarcane bagasse	IL dissolution	1:20 bagasse to AMIMCl at 110 °C, 5 h then 3 g PA added at 90 °C, 90 min	3.5	21	133	–	3	(M. J. Chen & Shi, 2015)
Mulberry wood	kneading	DMSO BMIMAcO, 9:5:1	12.1	–	56	138	3	(J. Chen et al., 2015)

[a] TS: tensile strength,.

[b] EB: elongation at break, FS: flexural strength.

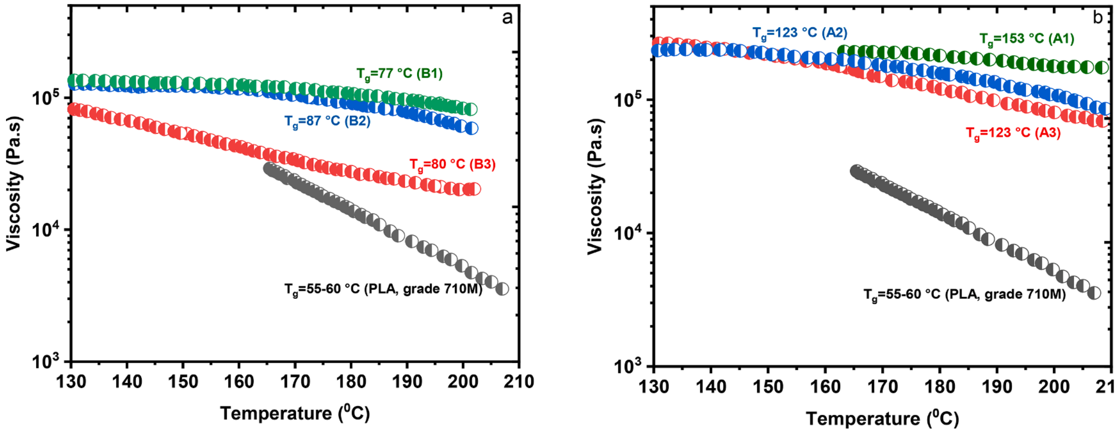

Fig. 7. Viscosity-temperature relationship of PLA (shear rate: 0.4 s^{-1}) (Tammaro, 2022) and thermoplastic lignocellulose (shear rate: 0.1 s^{-1}): (a) butyric anhydride and (b) acetic anhydride modified lignocellulose with varying T_g (J. Li et al., 2021a). (B3 and A1: molar ratio of sulfuric acid and Hyamine (benzethonium chloride) is 1.20. B1, B2, A3 and A2: molar ratio of sulfuric acid and Hyamine is 0.95). Drawn after (J. Li et al., 2021a; Tammaro, 2022).

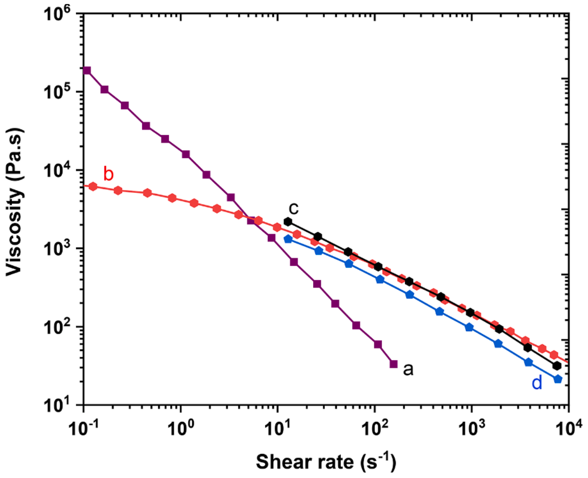

Fig. 8. Viscosity – shear rate relationships of (a) acetylated lignocellulose pulp at 120 °C (b) LDPE at 150 °C, (c) WPC (wood/polypropylene ratio: 40/60) at 180 °C and (d) WPC (wood/polypropylene ratio: 20/80) at 180 °C (Wilczyński & Buziak, 2021). The viscosity of acetylated lignocellulose was measured using rotational rheometer while capillary rheometer for LDPE and WPC. Redrawn from: (a) Li et al., 2021b, (b) Zatloukal, 2016, (c) and (d) (Wilczyński & Buziak, 2021).

and melt processability of modified lignocellulose materials. However, literature data on rheological behavior of thermoplastic lignocellulose materials are very limited.

5. Factors affecting the processing of thermoplastic lignocellulose material

5.1. Processing conditions

Most commonly NaOH is used to swell the lignocellulosic biomass and create a rough surface, and it also plays an important part in the activation step for functionalization/modification during thermoplastic lignocellulose development. Studies on bamboo fibers show that using a low concentration of NaOH (less than 5%) have little effect on its microstructure, whereas a higher concentration, above 10%, leads to the separation of the fibers from the fiber bundles and also the destruction of the middle fiber lamella (removal of lignin and hemicellulose) (J. Chen et al., 2014). Similar effects have been reported for different types of lignocellulose biomass (Borchani et al., 2015; Wang et al., 2015; López Durán et al., 2018a; Gao et al., 2021; Li et al., 2022). Consequently, the NaOH treatment has significant effects on the final mechanical properties.

The drying procedure during the processing can also affect the final properties of the material. The tensile strength and elongation at break of glycerol-plasticized microfibrillated cellulose are strongly affected by the drying method after plasticization. Improvement of the tensile strength by more than four times (from 27 to 130 MPa) and a reduction in the elongation at break (from 29 to 12%) were observed after plasticization of microfibrillated cellulose with glycerol and subsequent drying in a hot press at 100 °C with a 0.15 MPa pressure, followed by air drying at room temperature for 24 h (Van Nguyen & Lee, 2021). The applied pressure at elevated temperature (during drying) reduces the amount of voids between fibrils and promotes the formation of hydrogen bonds between the microfibrils (Österberg et al., 2013; Van Nguyen & Lee, 2021).

Using ball milling, followed by NaOH (10% solution) treatment of wheat straw, destroyed the original straw structure and reduced significantly the amount of residual lignin and hemicellulose, leading to an excess of cellulose in the residues (Gao et al., 2021). This treatment led, however, to a reduced mechanical strength (Gao et al., 2021). The removal of hemicellulose and lignin and the destroyed fibers during pretreatment and functionalization are responsible for the reduced mechanical strength.

The use of a functionalizing agent as a flow aid and plasticizer after extruding the lignocellulose with water is emerging as a possible alternative to minimize fiber breakage during processing. The combined effect of extrusion and NaOH is shown in Fig. 9 (Tian et al., 2022). The initially bundled fibers starts to separate as the NaOH concentration increases, implying a penetration of NaOH into the fiber structure and removal of hemicellulose and lignin Tian et al., (2022).

As the concentration increased, the fibers disintegrated and then started to agglomerate at the highest (20%) NaOH concentration. The effect of the applied shear force on the microfibrils of acetylated and extruded lignocellulose pulp from Aspen wood is shown in Fig. 10 (Li et al., 2019). It is noticeable from the SEM images that the fibrils were damaged after extruding 7 times at 70% solid content (Fig. 10b), while the fibrils were preserved after extruding 5 times at 60% solid content (Li et al., 2019).

The effect of acetylation time on the microstructural surface of bleached soft wood kraft pulp, flax fiber and thermomechanical pulp fibers was investigated at room temperature (Boustani et al., 2015). The SEM images in Fig. 11 showed signs of fiber degradation already after 2 h in all three systems (Boustani et al., 2015). The degradation was more pronounced as the reaction time proceeds implying the defibrillation (Boustani et al., 2015). Retaining all the components and increasing the

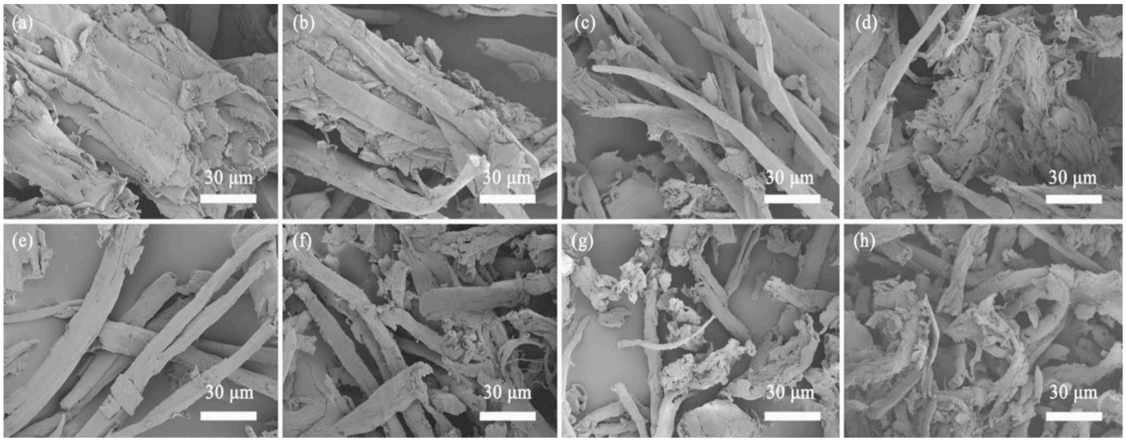

Fig. 9. SEM images illustration of the effect of extrusion on lignocellulosic fiber (a) native lignocellulose (b) screw extrusion without NaOH (c) after alkali extrusion pretreatment with 2.5 (d) 5.0 (e) 7.5 (f) 10.0 (g) 15.0 and (h) 20.0 wt% NaOH concentrations (Tian et al., 2022). Reproduced with permission from Springer Nature. Copyright 2022 Springer nature.

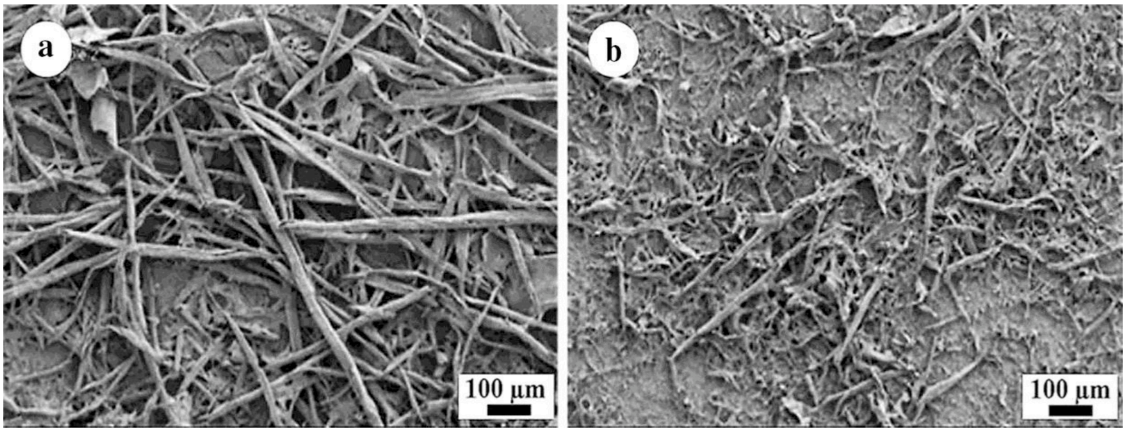

Fig. 10. Effect of extrusion on microfibrils of Aspen wood pulp (a) 60% solid content after 5 times extrusion (b) 70 solid contents after 7 times extrusion (Li et al., 2019). Reproduced with permission from Springer Nature. Copyright 2019 Springer nature.

reactivity and accessibility of each component in the fibers are important to introduce thermoplasticity in the entirety of the lignocellulose biomass, while maintaining mechanical strength.

5.2. *Thermal stability*

Fig. 12 shows modified lignocellulose materials, compression molded at 150 °C for butyric anhydride treated and 180 °C for acetic anhydride treated (J. Li et al., 2021a). The molded samples (Fig. 12a and b) showed well defined ages and smooth surfaces suggesting successful thermoplasticization of the modified lignocellulose, however, a change in color was observed after molding, indicating some degradation during the molding process (J. Li et al., 2021a). The change from light brown color to black color is indicative of aromatic oxidation during the molding process originating from the lignin component.

The effect of fiber dimensions on the thermoplastic material developed by modification of the entire lignocellulose biomass has hitherto not been studied. However, the effects are well studied in wood-plastic composite materials (Olakanmi & Strydom, 2016; Quijano-Solis et al., 2009; Quijano-Solis & Yan, 2014). Similar effects may, be expected also for more concentrated lignocellulose materials because of the higher shear force and higher melt temperature involved during thermal processing of the latter. This contributes to a more extensive fibers breakage and a resulting reduction in stiffness and strength. Therefore, the thermal processing conditions, such as extrusion screw speed, processing time and melt temperature are crucial to control to maintain the mechanical strength and stability of thermoplastic lignocellulose materials after modification for enhanced thermoplasticity.

6. Regulatory aspects of thermoplastic lignocellulose (biobased materials)

Even if plastic pollution is a major issue across the globe, there are no legal binding agreements and common consensus on a global level for regulating and developing policies on how to manage and deal with plastic waste. However, strong, and established strategies and policies are in place at regional levels to combat plastic pollutions, for example in EU. The EU adopted a plastic strategy in 2018 and is taking strong leading initiatives in integrating global efforts to tackle plastic pollutions (EU (COM), 2018). This paves a way for transitioning from fossil-based economy to circular economy, as outlined in the new circular economy action plan and the European Green deal (EU (COM), 2018, 2019, 2020). The effort bear fruit to develop common consensus at global level for regulating plastic pollution. Agreement were reached on negotiating and launching a legally binding agreement on plastic pollutions during UN Environmental assembly meeting in Nairobi, Kenya on March 2022 (EU Press, 2022). It is highly anticipated that by 2024 a global consensus will be reached among governments on the legal binding agreements, on how to avoid plastic pollution (EU Press, 2022). This accelerates the path for transitioning into circular economy

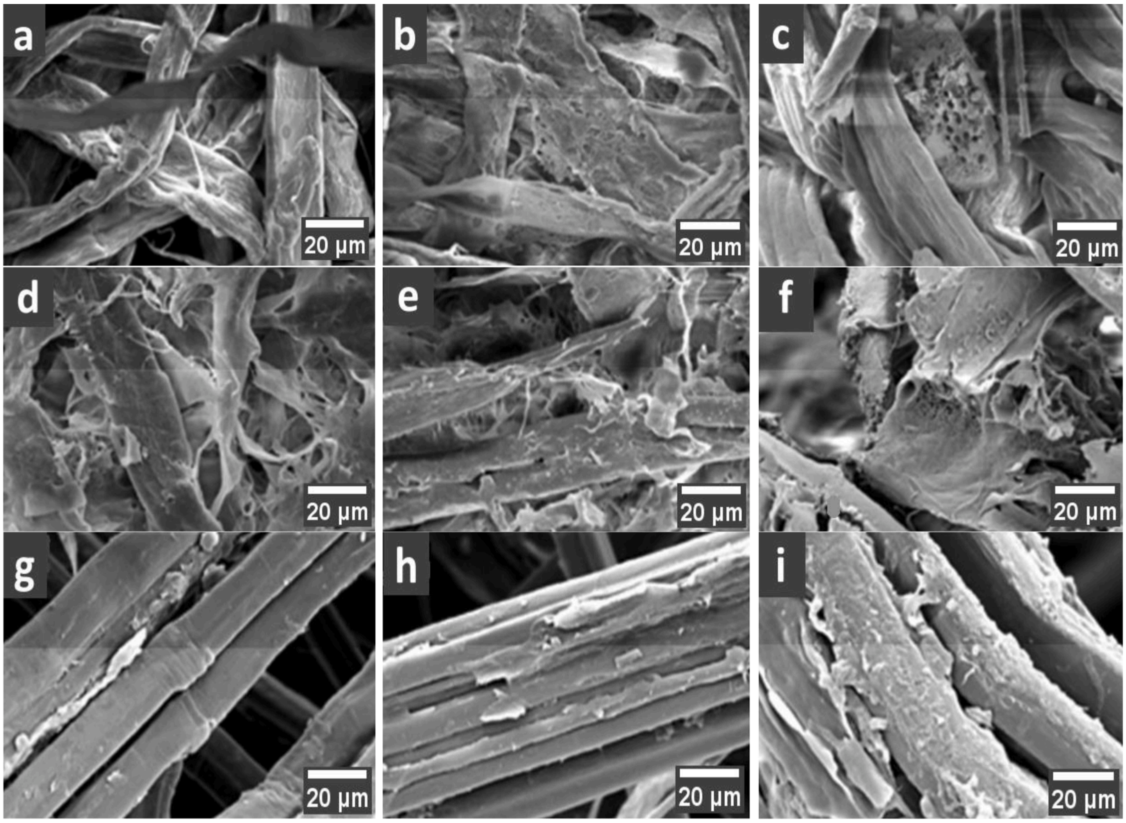

Fig. 11. Effect of acetylation time on fiber morphology: (a) untreated kraft fibers, (b) and (c) kraft fibers acetylated with acetic anhydride for 2 h and 24 h, respectively (d) unmodified TMP (thermo-mechanical pulp) fibers, (e) and (f) TMP fibers acetylated for 2 h and 24 h, respectively (g) unmodified flax fiber (h) and (i) flax fibers acetylated for 2 h and 24 h, respectively (Boustani et al., 2015). Reproduced with permission from John Wiley and Sons. Copyright 2015 Wiley Periodicals, Inc.

by positively affecting bio-based plastic production.

Achieving circularity in bioplastic production by substituting fossil-based plastics with sustainable and renewable materials, such as lignocellulosic biomass are one of the most prioritized sectors. However, biobased plastic products tend to be expensive and lacking some of the necessary properties such as hydrophobicity, extensibility, and flexibility compared to fossil-based counterparts. Therefore, narrowing down the tradeoff between fossil-based and biobased plastics are necessary to foster innovation and successful commercialization of thermoplastic lignocellulose. This might be achieved by policy interventions such as adopting stimulation policies. Odegard et al. (2017) suggested stimulation policy can accelerate the research and development of biobased plastics as done before in biofuel frontier (Odegard et al., 2017). They further suggested to develop consensus on a sustainability criteria and how to calculate CO_2 emissions and exploring ways of recycling biobased plastics (Odegard et al., 2017).

It is also important to emphasize the need for regulating the labeling on packaging materials, the use of “industrially compostable” instead of “biodegradable” and banning of oxo-degradable plastics, the latter has been enforced in New Zealand and EU (EU, 2018, 2019; Odegard et al., 2017; Order in Council, 2022). The use of languages and terminologies such as biodegradable, compostable, biobased plastics are confusing the customer and sometimes gives wrong impression about the products. The big misconception is the use of the term biodegradable, which seems to be reserved for biobased products, in fact there are biodegradable and non-biodegradable plastics from both biobased and fossil-based resources. The categories of biodegradable and non-biodegradable plastics from both biobased and fossil based plastics are well summarized in Fig. 13 (European Bioplastics, 2018). The term compostable is also vague, the condition under which it is compostable, whether home compostable or industrially compostable needs to be clarified and explained (Yadav & Hakkarainen, 2021).

The minimum percentage of bio-based content or renewable carbon content is another factor that needs to be clarified in order to classify composite products as biobased or not. This implies the need for competent institutions that work on standardization and authentications of the emerging products as if they are biobased or not. The regulatory and policy issues are perhaps more important to focus on for newly emerging biobased plastic families, such as those from thermoplastic lignocellulose. Lignocellulosic biomasses are modified entirely or partly to accommodate thermoplasticity and hence used as plastic substitutes. However, to our knowledge no specific and clear rules and regulations are in place for such type of new product families. It is necessary to regulate the used terminologies, the compositions, the types of additives and plasticizers added, recyclability, and setting lower limits on biomass content (percentage of biomass) for each product families in a more clear and specific way. In case of food packaging materials, the migration of components and the overall mass transfer between the food components and the packaging material is also key to understand in early stage of packaging material development. The recycling conditions and the risk of the generation of nano- and microplastics, even from biodegradable polymers, to the environment are also important to establish before the product saturates the market (Wei et al., 2021; Wei et al., 2022, 2022).

7. Challenges and outlook

The idea of developing a plastic product entirely from lignocellulose biomass by introducing thermoplasticity is currently an active area of research. But quantifying thermoplasticity is still a difficult task and many scholars use T_g to indicate thermoplasticity of a material (Müller et al., 2019; Li et al., 2021c, a; Tian et al., 2022). However, the

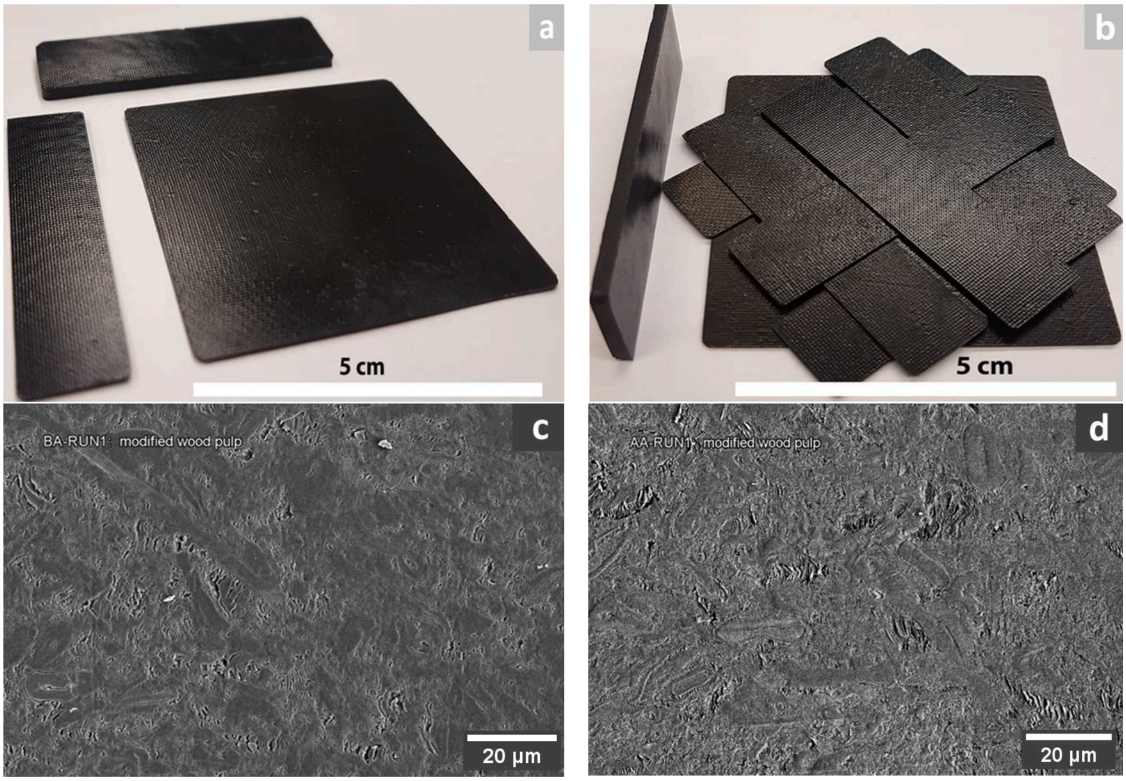

Fig. 12. Images of compression molded modified lignocellulose with (a) butyric anhydride (b) acetic acid anhydride and cross sectional SEM images of molded: (c) butyric anhydride and (d) acetic anhydride modified lignocellulose (J. Li et al., 2021a). Reproduced with permission from Elsevier. Copyright 2021 Elsevier.

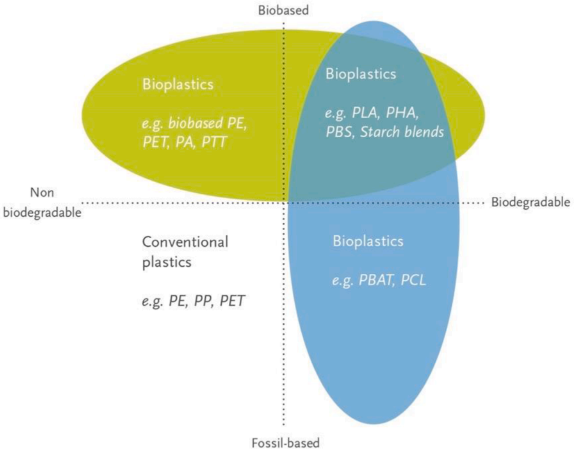

Fig. 13. Examples and classifications of biodegradable and non-biodegradable plastics from both biobased and fossil based plastics (European Bioplastics, 2018). Reproduced with permission from European Bioplastic.org. Copyright 2018 European Bioplastic.

processability of a biopolymer also depends on the actual melting temperature (for a semicrystalline polymer), melt viscosity and decomposition temperature (Müller et al., 2019). The larger the processing window, such as the interval between the T_g (or melting point) and the decomposition temperature, the easier it is to process the material in e.g., extrusion. The effect of fiber dimensions and the effect of each lignocellulose component (cellulose, hemicellulose, and lignin) on mechanical properties and thermoplasticity of modified lignocellulose materials are not yet fully studied. Pretreatment types such as grinding, milling, cutting and types of chemicals used (acid, alkali, ionic liquid) greatly affects the fiber dimensions and composition of the modified material. To achieve good flowability/thermoplasticity, the ideal fiber dimensions and compositions (% cellulose,% hemicellulose, and% lignin) in lignocellulose need to be determined. Since lignocellulose biomass differs in amount of chemical composition (cellulose, hemicellulose and lignin), it is important to develop specific modification methods for specific types of lignocellulose (hardwood, softwood, agricultural residues) to attain good thermal processability.

Current approaches of lignocellulose modifications for improving thermoplasticity are mainly based on attaching modifiers and plasticizers on hydroxyl, carboxylic/carbonyl and methoxy sites, blocking lignin repolymerization/formation of C—C bonds, and depolymerization followed by repolymerization processes for allowing chain mobility and flowability in the entire biomass. It is also important to understand how and where the modification exactly occurs in the separate biomass fractions, which is often not disclosed/reported, given the resemblance between cellulose and hemicellulose molecular structure. Plasticizers are often added to improve the flowability and flexibility. This changes the viscosity and rheological behaviors of the modified lignocellulose, as well as decreasing T_g. Studies on rheological properties of thermoplastic lignocellulose are currently very limited and it is important to focus on the rheological properties to get a full image on the thermal processability of thermoplastic lignocellulose. Likewise, the correlation between the modification chemistry and the final rheological/mechanical properties are often not fully understood/researched, which is important to develop future lignocellulose materials with improved thermoformability/thermoplasticity.

The growing concept of sustainable development and pressing issues of climate changes, opens the way for thermoplastic lignocellulose, which have a good potential to replace fossil-based plastics. Utilizing lignocellulosic biomass for bio-based plastics production avoids the competition with food production, since lignocellulose biomass grows in areas of non-agricultural lands and is also obtained from forest and agricultural residues (Álvarez-Chávez et al., 2012). The current status of the product has a promising future taking into account the sustainability, renewability and abundance nature of the product. To fully understand the life cycle of thermoplastic lignocellulose, detailed techno-economic analysis and environmental impact assessment are required. The feasibility study assesses the technical issues, market value of thermoplastic lignocellulose and related regulatory issues, which provides useful information for investors, policymakers, and regulators to take meaningful decision and implementation of the right strategies.

It is also important to note the importance of upscaling of thermoplastic lignocellulose production. Reactive extrusion is used for mixing, reaction and functionalizing medium, compromising altogether simplifications of the upscaling issues. Nevertheless, identifying proper reaction conditions, and type of solvents are necessary to obtain required flowability and processability. The use of existing conventional plastic production methods such as extrusion and injection or compression molding make the issues of up scaling easier, but detailed understanding and knowledge of large-scale processing needs to be assessed to know how the product behaves at large scale.

It is also important to control and minimize market manipulations (misrepresentation and misuse). Unintentional or deliberate misuse of terminologies to confuse customers, such as labeling of biodegradability for a product, which gives the impression of a biobased product needs to be controlled continuously. Therefore, clear rules and regulations and encouraging polices must be devised for thermoplastic lignocellulose (for each biobased plastic categories) to close the loopholes and build consumer trust and confidence.

8. Conclusion

This review article provides a state-of-the-art description of thermoplastic lignocellulose materials developed, with focus on materials with all the three major components of lignocellulose biomass still present. Modification strategies to turn lignocellulose biomass into thermoplastic materials are given. The processing (rheological and thermal) properties of these are discussed and compared to “conventional” thermoplastic materials (thermoplastics). Examples of the final mechanical properties of the thermoformed lignocellulose materials are given. Promising improvement and good progress have been made in thermoplastic lignocellulose development and several products have already entered the market in the form of e.g. molded wood-based materials (refer to Table 1). However, there is still a challenge to make lignocellulose materials as easily thermo-processable as the most common conventional thermoplastics (e.g. polyethylene). This is, at least partly, due to the often complex/heterogeneous nature of the former (e.g. the fibrillar structure). Another challenge is to improve the processability without changing adversely the final mechanical properties. A chemical modification, or the implementation of a lubricant/plasticizer, to improve the processability can have detrimental effects on the final mechanical properties. Yet another challenge is to improve the thermoplasticity of the lignocellulose material without rendering it a “plastic”, with the associated regulations. However, despite the challenges, the urgent need to replace fossil-based plastics with those that are biobased, makes it important to develop bioplastics from abundant renewable resources, such as wood.

CRediT authorship contribution statement

Bahiru Tsegaye: Conceptualization, Data curation, Visualization, Writing – original draft. **Anna Ström:** Conceptualization, Data curation, Writing – review & editing, Funding acquisition. **Mikael S. Hedenqvist:** Conceptualization, Data curation, Writing – review & editing, Funding acquisition.

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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