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This review focuses on the progress made over the last decade, in the development of bio-based matrices for biocomposite applications.

Graphical Abstract
50x50mm (300 x 300 DPI)

Matrices from Vegetable Oils, Cashew Nut Shell Liquid, and Other Relevant Systems for Biocomposite Applications

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TABLE OF CONTENTS

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1) Abstract

The partial replacement of petroleum-derived plastics and composites by novel bio-based materials from inexpensive, renewable, natural resources has the potential to greatly impact the plastics, coatings, and composites industries. Natural starting materials are usually abundant and renewable on a time scale many orders of magnitude smaller than petroleum. These characteristics, in combination with good mechanical properties, make the design of bio-based composites an interesting strategy for lowering the environmental impact of the plastics and composites industries while maintaining economical competitiveness. The present review will focus on the progress made over the last decade in the development of a select group of bio-based matrices for biocomposite applications. The text is organized into sections that describe a matrix system and its many reinforcements. The matrices covered in this review include composites from vegetable oils, cashew nut shell liquid, and a brief overview of other currently academically relevant bio-based matrix systems, such as polysaccharides, polylactide (PLA), polyhydroxyalkanoates (PHAs), proteins, and lignin.

2) Introduction

The partial replacement of petroleum-derived plastics and composites by novel bio-based materials from inexpensive, renewable, natural resources has the potential to greatly impact the plastics, coatings, and composites industries. Natural starting materials, such as vegetable oils, polysaccharides, lactic acid, polyhydroxyalkanoates, lignin, protein, and agricultural by-

products, are abundant and renewable on a time scale many orders of magnitude smaller than petroleum. Furthermore, new bio-based materials may exhibit similar and sometimes better properties than commercial petroleum-based products. [1] Because of these promising characteristics, the design of bio-based materials represents an interesting strategy for lowering the environmental impact of the plastics and composites industries while maintaining economical competitiveness. One topic that often comes to mind when discussing bio-based materials is biodegradability, and although the present review does not specifically focus on the biodegradability of composites, it is important to note that the rate of degradation of a material in the environment greatly depends on its intended application. For example, in the construction industry, long-lasting, non-biodegradable materials are desirable, whereas it would be very interesting for disposable goods, like golf teas and flower pots, to be made out of biodegradable, bio-based materials.

A variety of chemicals and materials are currently prepared from bio-based feedstocks.[2] A succinct list of examples includes bio-oil and syngas obtained from the pyrolysis of wood and agricultural waste streams;[3] protein-based biopolymers prepared from soybean and corn proteins;[4,5] and polylactide from the fermentation of polysaccharides.[6] In addition, vegetable oils are widely used in paints,[7] biocoatings,[8] and as building blocks for bio-based resins, such as polyurethanes,[9] polyester amides,[10] multi-component thermosets,[11,12] and cyanate esters.[13] In fact, 15% of all soybean oil produced from 2001 to 2005 was used in such applications.[14] Some of these systems were reinforced with nanoclays,[15] glass fibers,[16] and natural fillers.[17, 18]

The aforementioned bio-based materials can be reinforced with inorganic fillers or natural fibers to form bio-based composites.[19, 20] Such materials, and other similar composites reinforced with biomass, represent a remarkably simple technology that has great potential for applications in the

automobile, construction, and furniture industries.[21,22] In fact, renewable oils-based polymers are already a reality in the current coating, and composite markets.[21]

The present review will mainly focus on the progress made over the last decade in the development of a select group of bio-based matrices for biocomposite applications. Biocomposites created by the incorporation of biorenewable reinforcements into synthetic polymer matrices have become well established, and there are many reviews in the literature covering this topic.[23,24,25] Another well-documented aspect is the surface modification of natural fibers for composite applications.[26,27,28] Although there has been some progress towards manufacturing completely biorenewable composites over the last decade, relatively little attention has been paid to biorenewable matrices, and the topic is either only partially covered in the recent literature,[19,20] or the available reports only focus on a narrow and very specific type of matrix.[29,30,31,32,33] In this review, we emphasize biorenewable matrices, which we expect to become more important as the demand for completely biorenewable composites increases. The text is organized into two major sections, one dedicated to thermosetting matrices, and another one covering thermoplastic matrices. These two major sections are subdivided according to specific matrix systems. For each one of these matrices, a thorough description of the system and its many reinforcements is provided. The matrices covered were chosen based on the authors' areas of expertise[34] and include composites from vegetable oils, cashew nut shell liquid, and an overview of other currently relevant bio-based matrix systems, such as polysaccharides, polylactide (PLA), polyhydroxyalkanoates (PHAs), proteins, and lignin. In order to help the reader better follow along the different systems covered in this manuscript, a Table containing all of the acronyms employed in this review is provided (Table I).

Table I. Acronyms used in this manuscript.

Acronyms	Explanation
ADMET	acyclic diene metathesis
AESO	acrylated epoxidized soybean oil
BMA	*n*-butyl methacrylate
CCO	conjugated corn oil
CLO	conjugated linseed oil
CLS	conjugated low saturation soybean oil
CNSL	cashew nut shell liquid
COR	corn oil
CSO	conjugated soybean oil
DCPD	dicyclopentadiene
DSC	differential scanning calorimetry
DVB	divinylbenzene
HMTA	hexamethylenetetramine
MA	maleic anhydride
MAESO	maleated acrylated soybean oil
MDEA	N-methyl diethanol amine
MDI	methylene diphenyl diisocyanate
MSOL	methoxylated soybean oil polyol
P3HB	poly-3-hydroxybutyrate
PHA	polyhydroxyalkanoate
PHO	polyhydroxyoctanoate
PLA	polylactic acid
PUD	polyurethane dispersion
ROMP	ring opening metathesis polymerization

5

SEM	scanning electron microscopy
SOY	soybean oil
ST	styrene
TEM	transmission electron microscopy
TPS	thermoplastic starch
TUN	tung oil
WAX	wide angle X-ray diffraction

3) Thermoplastic Matrices

a) Vegetable Oils

Vegetable oils consist of triglycerides of various fatty acid compositions (Figure 1). Distinct vegetable oils exhibit fatty acid chains with different chain lengths. In addition, the number and the position of the carbon-carbon double bonds varies along the fatty acid chains of different oils, and in some cases functional groups may be present.[35]
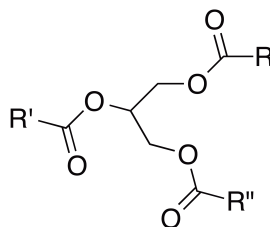

Figure 1. Chemical structure of a generic trigliceride, where R, R', and R″ are hydrocarbon

chains.

In recent years, a variety of vegetable oil-based polymers with versatile thermal and mechanical properties were prepared by free radical or cationic polymerization of regular and modified vegetable oils in the presence of petroleum-based comonomers.[36,37] In these systems, the carbon-

carbon double bonds constitute the reactive sites. When the carbon-carbon double bonds are conjugated, the oil exhibits an overall increased polymerization reactivity.[38] Here, the term "conjugated oil" designates oils in which the vast majority of the carbon-carbon double bonds are conjugated. Recently, other polymerization methods, such as ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET), were also employed to synthesize vegetable oil-based polymers.[39,40]

A commercial grade of acrylated epoxidized soybean oil (AESO) was copolymerized with styrene in the presence of a mixture of multi-walled carbon nanotubes and soot.[41] For nanotube loadings lower than 0.28 wt.%, the resulting composites exhibited significant improvement of their mechanical properties in comparison to the pure resin. At higher load levels, agglomeration of carbon nanotubes resulted in a decrease in mechanical properties.[41,42] A comparison of the mechanical properties of these and other select vegetable oil-based composites discussed in this section is shown in Table II. For comparison purposes, the tensile and flexural properties of glass, and carbon fiber/epoxy composites are displayed in Table II (entries 1 and 2). Although the tensile modulus of these composites is significantly higher than that of all vegetable-oil biocomposites covered in this review (entries 3-10), for certain combinations of bio-based resin and natural filler (entries 4 and 5), comparable values are obtained for the tensile strength and the storage modulus of petroleum- and bio-based composites at much lower natural filler loadings.

Table II. Mechanical properties of select vegetable oil-based biocomposites.

Major Resin Component (wt.%)	Reinforcement (wt.%)	Modulus (GPa)	Strength (MPa)	Storage Modulus (MPa)	Reference
Epoxy (100)	Glass fibers (70)	40-45/tensile	55-800/tensile	2700 at 25 ˚C	-
Epoxy (100)	Carbon fibers (70)	181/tensile	-	2340 at 25 ˚C	-
AESO (65)	Carbon nanotubes (1)	-	-	1516 at 35 ˚C	42
AESO (67)	Keratin + glass fibers (30)	1.9/flexural	58/flexural	2085 at 40 ˚C	44
AESO (50)	Flax + glass fibers (40)	5.2/tensile 9/flexural	129/tensile 206/flexural	-	45
Maleinated acrylated epoxidized soybean and linseed oils (70)	Red oak leaves (11)	-	-	1289 at 30 ˚C	48
CCO (65)	Glass fibers (21)	1.0/tensile	8.3/tensile	-	49
Low saturation soybean oil (50)	Glass fibers (50)	2.7/tensile	76/tensile	-	50
CCO (50)	Modified montmorillonite clay (3)	0.2/compressive	32/compressive	-	53
Tung oil (50)	Spent germ (45)	0.8/tensile 1.1/flexural	15.1/tensile 25/flexural	1434 at 25 ˚C	54
CSO (50)	Soybean hulls (50)	0.7/tensile	2.3/tensile	686 at 25 ˚C	55

AESO-based resins were also reinforced with keratin fibers from chicken feathers for the preparation of biocomposites to be used as printed circuit boards.[43] The low dielectric constant obtained for these materials was a result of entrapment of air in the keratin fiber structure during

8

the synthesis of the composites.[44] Synergistic effects on the flexural and impact properties of AESO-based composites were observed when glass and flax fibers were used as reinforcements,[45] and materials with promising properties for applications in the construction industry were prepared by the reinforcement of AESO resins with cellulose, pulp, hemp, and recycled newspaper.[46] The use of butyrated lignin as a compatibilizer between polyAESO-co-polystyrene and flax fibers was successfully demonstrated.[47] A similar composite system, a commercial maleated acrylated epoxidized soybean oil (MAESO)/styrene resin was successfully reinforced with dewaxed red oak leaves.[48]

Cationic copolymers of corn oil (COR), styrene (ST), and divinylbenzene (DVB) were successfully reinforced with up to 45 wt.% of continuous glass fibers, resulting in significant improvements in Young's modulus and tensile strength compared to the unreinforced, vegetable oil-based matrix.[49] Changes in the concentration of the resin components also affected the mechanical properties of the composites.[49] In fact, it was observed that increases in the DVB content resulted in an increase in crosslinking density, which had an overall positive impact on the material's properties. Also, the replacement of COR with conjugated corn oil (CCO) resulted in a material with slightly better properties.

When up to 50 wt.% continuous glass fibers were added to soybean oil (SOY)-based cationic resins, significant increases in Young's modulus and tensile strength were obtained.[50] Glass fibers were also used to reinforce copolymers obtained by the ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) and dilulin (the product of the Diels-Alder reaction of linseed oil with cyclopentadiene).[51] Because the presence of glass fibers does not affect the crosslinking density of the resin, neither changes in T_g values nor in thermal stability were detected when the pure resin was compared to the reinforced composite.[51] Despite

9

a significant increase in Young's modulus after addition of the fibers, an SEM study revealed only a weak interaction between the matrix and the reinforcement.[51]

Vegetable oil-based composites were also prepared by the addition of organo-modified montmorillonite clay to the aforementioned vegetable oil-based resins.[52] Cationic thermosets were prepared by copolymerization of either conjugated soybean oil (CSO) or conjugated low saturation soybean oil (CLS) with ST and DVB. Wide angle X-ray diffraction (WAX) revealed the degree of nanoclay exfoliation in the composites, and transmission electron microscopy (TEM) imaging showed that their morphology greatly depended on the amount of nanofiller added, with an intercalated and exfoliated morphology at organoclay loadings ranging from 1 to 2 wt.%.[52]

Similarly, organo-modified montmorillonite clay was used as a reinforcement for corn oil-based cationic resins, resulting in an improvement in mechanical properties compared to the pure resin.[53] The resin consisted of a copolymer of CCO, ST, and DVB. In this system, optimum properties were obtained for clay loadings between 2 and 3 wt.%.[53]

With the new trend on the use of biorenewable materials, bio-based composites with higher biorenewable content were prepared by reinforcing vegetable oil-based thermosetting resins with spent germ,[54] soybean hulls,[55] corn stover,[56] wheat straw,[57] rice hulls,[18] wood flour,[58] oat hulls,[59] and sugar cane bagasse.[60] In these composites, peroxides were effective free radical initiators for the polymerization of the carbon-carbon double bonds in the oils and in the other comonomers [DVB, *n*-butyl methacrylate (BMA), and maleic anhydride (MA)]. A switch to free radical polymerization was necessary because the ligno-cellulosic fillers, which are naturally hydrophilic, rapidly quench the strong Lewis acids used to initiate the cationic polymerization process. During compression molding, the presence of ligno-cellulosic filler particles minimized

shrinkage of the resin, and only minimal micro-cracks were detected by scanning electron microscopy (SEM) of the soybean hull composites.[55] In a constant search for improvements in mechanical properties, recent studies of natural filler-reinforced composites suggested that MA is a good filler-resin compatibilizer and therefore helps to improve the thermo-mechanical properties of the composites.[56,58,61]

Different particle sizes of spent germ were used to reinforce a tung oil (TUN)-based resin that was cured in the presence of *t*-butyl peroxide.[54] The resin contained 50% of TUN, BMA, and DVB.[54] When compared to the storage modulus of the pure resin, the composites exhibited higher storage moduli.[54] The incorporation of shorter filler particles and higher DVB content resulted in better properties.[54] When the filler load was increased from 40 to 60 wt.%, agglomeration and formation of micro-voids in the composite caused an overall decrease in mechanical properties and an increase in wear depth against a diamond tip.[54,62] However, recent findings have shown that it's possible to compensate for this effect by an increase in molding pressure during processing.[54] It was also found that residual corn oil from the spent germ acted as a plasticizer in the composite. Removing the oil prior to impregnation of the fillers with crude resin resulted in better mechanical properties.[54,62]

In a similar manner, a CSO-based free radical resin was reinforced with soybean hulls.[55] The concentration of resin comonomers, BMA, DVB, and DCPD was varied, as was the filler particle size, the filler load (50 - 60 wt.%), and the molding pressure.[55] The concentration of CSO in the resin was kept constant at 50 wt.%.[55] An optimum cure sequence of 5 hours at 130 °C, followed by a post-cure of 2 hours at 150 °C was established after differential scanning calorimetric (DSC) analysis of the composites.[55] When BMA or DVB were substituted by DCPD, the mechanical properties were compromised.[55] In this particular system, a decrease in properties

was observed when excessive molding pressure was applied.[55] The different reactivities of the comonomers used to form the matrix resulted in the appearance of two distinct T_g's, indicating that the resin was phase-separated.[55]

Free radical resins containing 50 wt.% of either CSO or conjugated linseed oil (CLO) and various amounts of DVB and BMA were reinforced with 20-80 wt.% of corn stover.[56] Increasing the amount of corn stover and decreasing the length of the fibers resulted in an overall improvement in mechanical properties and in a decrease in thermal stability.[56] Water uptake experiments confirmed the expected direct relationship between water absorption and fiber content.[56] This characteristic of many natural fiber-reinforced composites is not necessarily detrimental. In fact, a higher filler load corresponds to a higher bio-based content, along with higher water uptake, which can be useful, for instance, in the recycling and disposal of the composite material.

Wheat straw was also used as natural filler in the preparation of bio-based composites.[57] Here, the resin consisted of a copolymer containing 50 wt.% CLO and various amounts of DVB, BMA, and MA.[57] Materials with bio-based contents up to 95 wt.% were obtained.[57]

A free radical resin composed of 50 wt.% CLO, 35 wt.% BMA, and 15 wt.% DVB was used to determine the optimal conditions for the preparation of rice hull composites.[18] In this case, 70 wt.% dried rice hulls, with particle sizes smaller than 1 mm in diameter, afforded the best composite properties.[18] Scanning electron microscopy (SEM), along with X-ray mapping of the fractured composites, revealed the presence of significant amounts of silica in the rice hulls, which may account for the high mechanical and thermal properties obtained.[18] With optimum parameters established for the preparation of rice hull composites, changes in resin composition were evaluated.[61] Composites made from CLO exhibited better overall properties than those

prepared from CSO, owing to the higher degree of unsaturation of CLO.[61] The same CLO-based free radical resin was also reinforced with switch grass. Improvements in mechanical properties of the composites were observed when increasing the filler load up to 70 wt.%. At higher loading levels, excessive agglomeration of the filler compromised the composite's properties.[63] A careful evaluation of the cure schedule of a similar resin reinforced with wood flour was carried out taking into account the necessary balance between filler integrity and a complete cure of the resin.[58]

A thorough study on the effects of different natural oils and different natural fillers on the properties of cationic composites was also carried out.[64] Cationic resins made from CSO, CLO, and CCO were reinforced with corn stover, wheat straw, and switch grass. All resins contained 50 wt.% oil, while the concentrations of ST and DVB were varied. The oils with a higher degree of unsaturation resulted in composites with better properties. With respect to the different fillers studied, wheat straw afforded composites with the most promising properties.[64] Overall, due to the great breadth of bio-based resins and reinforcements considered, the solutions to address certain issues faced in a particular system are created as the problems are detected and studied. Because these factors are extremely system-dependent, it is virtually impossible to have a single direction for the development and improvement of all vegetable oil-based composites.

Vegetable oils are used as the major components of coating formulations in the preparation of polyurethane dispersions (PUDs).[65] Despite the lack of thorough reports on their use as a polymer matrix in composite applications, the most recent progress in the area will be briefly highlighted here because of its increasing importance in the bio-based market. In fact, bio-based polyols can be obtained by ring opening reactions of the epoxide groups in epoxidized vegetable oils. Vegetable oil-based polyurethanes can be formed through the reaction of such polyols with

diisocyanates. Regular and modified castor oil and ricinoleic acid were used in the preparation of bio-based polyurethanes.[66,67] Polyols based on a variety of epoxidized oils (sunflower, canola, soybean, corn, and linseed oils) were polymerized with methylene diphenyl diisocyanate (MDI) to give polyurethanes.[68] Methoxylated soybean oil polyols (MSOLs), prepared by ring opening of epoxidized soybean oil with methanol, were used to prepare anionic waterborne PUDs.[69] Castor oil and methoxylated and acrylated epoxidized soybean oil-based polyols were reacted with N-methyl diethanol amine (MDEA) and MDI to form bio-based polyurethanes containing tertiary amines.[70] The protonation of amine groups resulted in waterborne cationic PUDs exhibiting very high adhesion to leather and glass.[70]

In order to increase their mechanical properties, soybean oil-based anionic PUDs were copolymerized with acrylic comonomers, resulting in polyurethane-acrylic hybrid latexes with 15–60 wt.% bio-based content.[71,72] Surfactant-free, core-shell hybrid latexes were synthesized by seeded emulsion polymerization of 10–60 wt.% of either ST or butyl acrylate in the presence of soybean oil-based PUDs.[73]

Other polycondensation systems involving vegetable oils include polyesters [74] and polyamides.[75,76] Nahar seed oil monoglyceride was reacted with phthalic and/or maleic anhydride to give polyesters with properties suitable for composite applications.[77] Likewise, copolyesters were obtained from the polycondensation and/or transesterification of ricinoleic acid and polylactide (PLA).[78,79,80] Recently, vegetable oil-based fatty amide monomers, such as fatty amide diols and castor oil amide-based α,ω-dienes, were utilized to prepare polyamides by esterification and ADMET polymerization, respectively.[75,76]

b) Cashew Nut Shell Liquid

Cashew nut shell liquid (CNSL) is an important agricultural by-product of cashew nut and cashew apple production, both of which are produced by the cashew nut tree (*Anacardium occidentale*).[81] Natural CNSL is a mixture of phenolic compounds with aliphatic side chains, including anacardic acid, cardanol, and cardol (Figure 2).[82] CNSL can be extracted by several methods including by hot oil process,[82] solvent extraction,[83] mechanical extraction,[83] vacuum distillation,[84] or supercritical fluids.[84] The overall composition of CNSL can vary based on the method of extraction.[82,85] During commercial processing, CNSL is typically treated with high temperatures, which decarboxylate anacardic acid, yielding cardanol as shown in Figure 3.[86] Additional distillation of the CNSL removes cardol, leaving cardanol as the primary component of CNSL.[86]
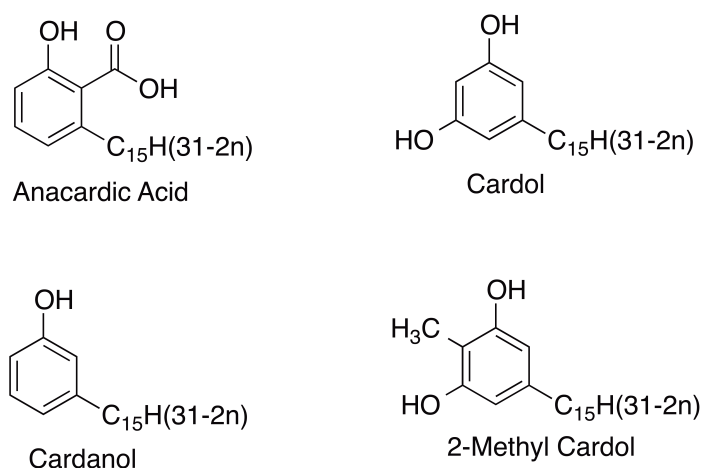

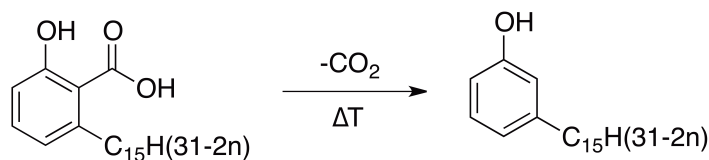**Figure 2.** Major components of cashew nut shell liquid, where n = 0, 1, 2, or 3.

Figure 3. Conversion of anacardic acid to cardanol, where n = 0, 1, 2, or 3.

The unique chemical properties of CNSL have enabled it to be employed in a wide range of applications. CNSL is one of a limited number of aromatic bio-based compounds that are economically feasible for use in industrial applications.[87] The aromatic rings in CNSL impart greater thermal stability enabling CNSL to be used in flame-retardant materials.[88] The phenolic structure of CNSL is known to have medicinal,[89] antioxidant,[90,91] and antimicrobial properties.[92,93] Several reviews have been written on the use of CNSL for applications in polymer synthesis,[82,94] olefin metathesis,[95] and fine chemicals.[86]

The different constituents of CNSL, as aromatic, phenolic compounds, can react with formaldehyde to create condensation polymers, such as resoles and novolacs, which make excellent matrix resins for composites.[87,96] Furthermore, the unsaturation sites in the side chains of CNSL can also undergo addition polymerization using either free radical initiators or ionic initiators.[97,98] Hexamethylenetetramine (HMTA) has been added as hardener to CNSL-formaldehyde resins as a method of improving the cure characteristics.[99]

Although phenolic-formaldehyde resins based entirely on CNSL have shown decreased mechanical properties compared to conventional phenol-formaldehyde resins, a number of different approaches have been explored for minimize the performance differences.[100] To minimize the reduction in mechanical properties, mixtures of cardanol and phenol can be copolymerized together with formaldehyde.[96,100] In one reported study, observed decreases in tensile and flexural strength were marginal in phenol-cardanol ratios up to 4-6 mol % cardanol,[100] whereas another study reported optimum performance with 40 wt.% cardanol substation of phenol.[96] Another strategy for improving the mechanical properties is to blend the CNSL-based resins with conventional resins. For example, cardanol-based novalac resins (5-10 wt %) have been used a compatible modifier with bisphenol A epoxy resins.[101] The resulting

resin blends had higher tensile strength, energy absorption at break, and water resistance compared to unmodified epoxy resins.[101] Chemical modifications of CNSL-formaldehyde resins have also been examined. For example, CNSL-based epoxy resins have been synthesized by chemical modifying CNSL-formaldehyde resins with epichlorohydrin.[87] The resulting epoxy resin was then reacted with methacrylic acid to prepare CNSL-based vinyl ester resin.[87]

Recent progress has been made in developing applications for CNSL-based resins. Resole resins made from CNSL show promise for reducing the overall cost of particle boards by replacing high cost synthetic resins.[102] Composite pipes have been made by using jute fibers to reinforce an epoxy resin, which was crosslinked with cardanol-based novolac.[103] Roofing panels have been prepared from CNSL-based resols using sisal fiber[104] and oil palm fibers reinforcements.[105] Clay (30-35 wt.%) has been incorporated into the CNSL-based natural fiber composites as way to further improve the mechanical properties (i.e. tensile strength, flexural strength) for low cost roofing materials. [105]

CNSL, as well as other materials generated as food supply chain waste, has garnered attention as a valuable, but underutilized resource for higher value applications.[106] CNSL has been identified as an ideal matrix material especially in underdeveloped areas of the world where cashews are grown. While standard fillers like glass fiber mats have been used with CNSL-based matrices,[107] there is growing interest in developing CNSL-based composites using natural fillers, which are readily available locally. Examples of natural fibers that have been used to reinforce CNSL-based novalac or resole type resins include oil palm fibers,[105] sisal fibers, [108] kenaf, [109] hemp bast fibers, [109] butiri fibers, [110] jute fibers,[111] and coconut coir fibers.[112] Other renewable fillers include rice husks, [113] coffee husks, [114] and sawdust.[102]   Natural fibers reinforcements are frequently pretreated with an alkali solution (i.e. 5 to 12% sodium hydroxide solution), which is

17

also called mercerization, to increase the number of hydroxyl groups on the surface of the fiber.[108,109,110,111] The composite properties are improved due to the interaction between the hydroxyl groups and the polar matrix.[110] A comparison of the mechanical properties of selected CNSL-based composites, is shown in Table III.

Table III. Mechanical properties of select CNSL-formaldehyde composites.

Resin Type	Reinforcement (wt.% or v%)	Treatment	Modulus (GPa)	Strength (MPa)	Storage Modulus (MPa)
Novalac[a]	Hemp fibers	6% NaOH	13/flexural	91/flexural	~800 at RT
Novalac[a]	Kenaf fibers	6% NaOH	17/flexural	166/flexural	~1000 at RT
Resol[b]	Coconut coir (20 v%)	Raw	10.5 / tensile	6.42/tensile	-
Resol[b]	Coconut coir (20 v%)	5% NaOH	16.9 / tensile	13.45/tensile	-
Resol[b]	Coconut coir (20 v%)	10% NaOH	20.4/tensile	18.21/tensile	-
Resol[c]	Jute fibers ()	5% NaOH	-	23.47/tensile	-
Resol[c]	Jute fibers	10% NaOH	-	6.56/tensile	-

a. Data adapted from Ref 109. b. Data adapted from Ref 112. c. Data adapted from Ref 111.

One of the most promising new applications of CNSL is the development of cardanol-based polybenzoxazines (Figure 4). [115,116] Benzoxazines are synthesized by a Mannich-like condensation of a phenol, formaldehyde, and primary amines.[117] Polybenzoxazines represent a significant improvement over conventional phenol formaldehyde resins because no by products are released during curing.[117] Polybenzoxazines are known for their excellent physical and mechanical properties, including low water absorption, chemical resistance, and minimal shrinkage; they also offer excellent thermal properties and flame retardance because of their phenolic structures. [118,119] Applications of polybenzoxazines include their use in high-

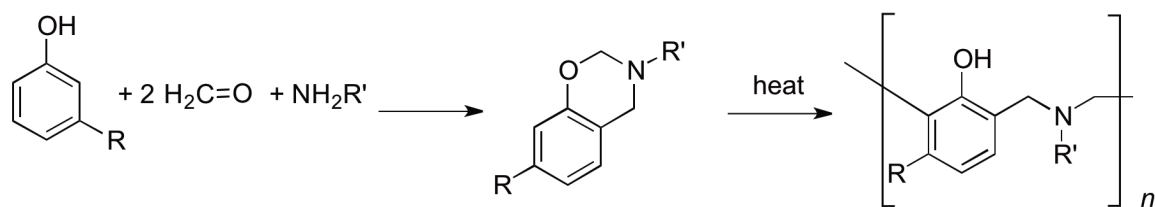performance polymers and advanced composites, such as those found in the aerospace and automotive industries.[119,120]

Figure 4. Cardanol-based polybenzoxazine. R = $C_{15}H_{31-n}$, where n = 0, 2, 4, or 6 based on the unsaturation of side chain. R' can vary based on the selection of the primary amine.

Due to the versatile molecular design of polybenzoxazines, a wide range of approaches has been proposed for synthesizing and CNSL-based polybenzoxazines resins and composites. Similar to phenolic-formaldehyde resins described previously, CNSL-based polybenzoxazine resins have been blended with other resins, such as bisphenol A-based polybenzoxazine resins, in order to improve their performance.[121] A limited number of studies have incorporated furan groups as a performance enhancer by using furfural modified cardanol[122,123] for the synthesis of furfural-CNSL-based polybenzoxazines.[124,125] Other studies have reported modifying bisphenol A-based benzoxazines by alloying with cardanol with the polybenzoxazine after the benzoxaxine synthesis is completed.[126,127] In the polybenzoxazine-CNSL alloys,[126,127] the oxazine rings react with the phenolic rings found in CNSL during thermal curing.[120]

Another target for modification of polybenzoxazines is the selection of the amine, which can be either aromatic or aliphatic. Aniline[121] and ammonia[115] are examples of amines that have been used to make CNSL-based polybenoxazines. More recently, bifunctional bisbenzoxazines have been made by reacting monofunctional phenols and diamines together with formaldehyde.[128] Cardanol-based bisbenzoxazines have been made with various aromatic diamines such as bis-(4-

(4-aminophenoxy)phenyl)ether, 4,4'-diaminodiphenylsulphone, and 2,2-bis(4-(4-aminophenoxy)phenyl)propane.[128]

Conventional fillers, like glass fabrics, have been used with CNSL-based polybenzoxazine resins and alloys.[121] Biorenewable fillers have also been used such as jute fibers,[115,116] flax fibers,[129] wood flour,[130] eastern red cedar wood particles,[127] and bamboo fibers.[126] Fiber treatment is another potential target for improving the performance of CNSL-based polybenzoxazines.[115] The mechanical properties for a selection of CNSL-based polybenzoxazine composites are listed in Table IV. The information listed in the table should be viewed only as an illustration of the general properties of CNSL-based polybenzoxazines due to the wide variation between the reported studies in formulation and processing conditions.

Table IV. Mechanical properties of select CNSL-based polybenzoxazines.

Starting Material	Resin Type	Amine	Reinforcement (wt.%)	Modulus (MPa)	Strength (MPa)	Storage Modulus (MPa)
Cardanol[a]	Benzoxazine	Ammonia	Untreated jute (33)	4890/tensile	20.6/tensile	-
Cardanol[a]	Benzoxazine	Ammonia	NaOH treated jute (26)	2006/tensile	13.07/tensile	-
Cardanol[b]	Benzoxaxine	Aniline	Neat (0)	-	-	278 at 38° C
Cardanol[b]	Benzoxaxine	Aniline	Untreated jute (30)	-	-	694 at 37 °C
Cardanol[b]	Benzoxaxine	Aniline	Acrylonitrile modified jute (30)	-	-	1419 at 37 °C
Technical CNSL[c]	Bis(benzoxazine)	4,4'-diaminodiphenyl methane	Neat (0)	-	-	440 at RT
Technical	Bis(benzoxazine)	4,4'-	Wood flour	-	-	900 at RT

CNSL[c]		diaminodi phenyl methane	(30)			
Technical CNSL[c]	Bis(benzoxazine)	4,4'- diaminodi phenyl methane	Wood flour (50)	-	-	1100 at RT

[a.] Data adapted from Ref 115. [b.] Data adapted from Ref 116 [c.] Data adapted from Ref 130.

4) Thermoplastic Matrices

a) Polysaccharides

Polysaccharides are one of the most important types of renewable materials available. They have traditionally been used for food, clothing, paper, lumber, and fuel.[131] Of the numerous examples of polysaccharides, the three most important for use as biorenewable materials are starch, cellulose, and chitin.[132] All three of these polysaccharides can be used as matrices for composites. More recently, polysaccharides from seaweed, including agar and alginate, were used as biorenewable matrices for composites. Bacterial polysaccharides, such as xanthan gum, were used as bio-based matrices, but are not included in the scope of this review.[133] However, not all common polysaccharides are useful as biorenewable matrices. Glycogen, a highly soluble and amorphous polysaccharide, has limited value for commercial uses. Hemicelluloses are not typically used in industrial applications because of their low thermal stability and high hydrophilicity.[134,135]

Starch

Starch is the major form of carbohydrate in plants, occurring as a mixture of highly branched amylopectin and linear amylose. Amylopectin consists of linear D-glucopyranose chains linked by O-α-(1→4) glycosidic bonds and branching occurring as O-α-(1→6) glycosidic bonds. Amylopectin is a brittle biopolymer. In contrast, amylose has O-(1→4)-α-D-glucan linkages and

21

is film-forming. When exposed to high temperatures and in the presence of a plasticizer, starch exhibits similar melt and flow characteristics as regular synthetic thermoplastic. Glycerol is the standard plasticizer added when processing thermoplastic starch (TPS).

One major drawback of TPS is the fact that it is prone to excessive hydrophilicity, which compromises its otherwise very promising mechanical properties. [136] To counteract the hydrophilicity of starch, hydrophobic fillers, such as montmorillonite nanoclays, were used with starch matrices to reduce water affinity.[136] Although natural clays are more prevalent, synthetic nanoclays, such as synthetic beta zeolite and Na-beidellite, were examined as fillers.[137] Similarly, the use of lanthanum hydroxide nanoparticles as fillers in TPS-based composites resulted in materials with improved mechanical properties while decreasing the undesired excessive hydrophilicity of TPS.[138] In another approach to overcome the hydrophilicity of TPS, composites were prepared with synthetic polymers, such as low density polyethylene.[139] Natural cellulose fibers, when used as reinforcement in TPS composites, afforded composite materials with improved water resistance, thermal stability, and higher tensile strength.[140]

A major application of TPS is the production of foamed materials for loose-fill packing. [141]Starch composites are being explored to produce packaging materials with improved properties. In particular, composites with low cost, biodegradable fillers, such as soy pulp, are being investigated as packaging and other disposable items.

Composites with 10 wt.% soy pulp filler showed increased tensile strength and flexural strength.[142] In fact, starch-based nanocomposites were prepared by the reinforcement of starch with a variety of organic (cellulose) or inorganic (clays) nanoparticles.[143] A thorough discussion of methods for the improvement of filler and matrix interactions was recently published.[143] In a related research, recycled paper cellulose fibers from office paper and newspaper were used to

make biodegradable composites with higher mechanical properties than TPS.[144] Fibers from natural sources, such as cotton, hemp, kenaf, and sugar cane bagasse, were used as reinforcement in order to improve thermal and mechanical properties.[145,146,147] Laponite, a synthetic mineral similar to natural hectorite, was used as a filler with thermoplastic starch to produce nanocomposites with improved thermal stability and mechanical properties.[148]

Cellulose

One of the most important biorenewable materials in composites is cellulose, which is typically used as a natural replacement for glass fibers.[149] The use of cellulose fibers in composites has been extensively investigated and reviewed.[150] Thus, the use of cellulose fibers is only briefly mentioned in this review. Cellulose fibers can be used with or without modifications. However, cellulose is often physically or chemically modified to improve adhesion between the fibers and the matrix.[151,152,153,154,155,156]

Cellulose is a natural material found in the cell walls of plants along with other polysaccharides, including pectin and hemicelluloses.[157] Cellulose is a linear polysaccharide comprised of *D*-glucose linked by $\beta(1\rightarrow4)$ glycosidic bonds.[157] A depiction of the chemical structure of cellulose commonly used is shown in Figure 5. The cellulose present in the wood harvested from forests is a major source of fuel and lumber.[158] It is worth mentioning that the sustainable harvesting of wood from forests is environmentally friendly and carbon neutral.[158]
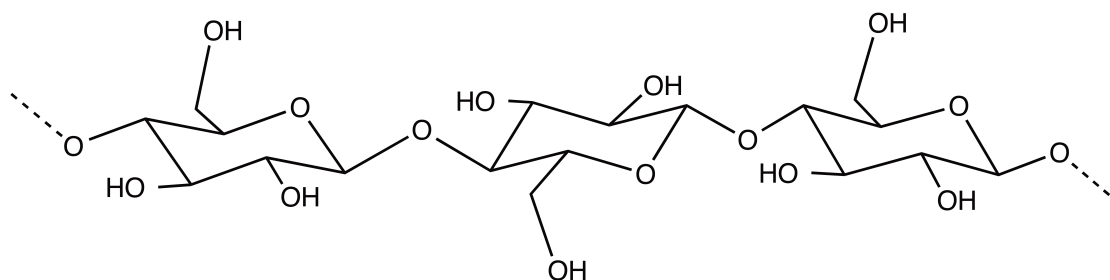
23

Figure 5. Structure of cellulose.

Cellulose composites containing cellulose fillers and a cellulose matrix were prepared by several different approaches.[159] A key criterion for the successful preparation of all cellulose composites is to differentiate the solubility of cellulose when it's employed as the matrix from when it's used as reinforcement.[160] Often, solubility differentiation can be achieved by pretreatment.[161]One straightforward method is to disperse cellulose nanoparticles, such as acetylated cellulose nanowires, in cellulose acetate, followed by casting into a gel and evaporating the liquid.[159] It has been shown that cellulose nanocomposites can be generated by drying a solution of cellulose in ionic liquid after adding nanocrystalline cellulose to it.[162]

Hybrid composite materials comprised of cellulose-based matrices and metal particles were evaluated for their antimicrobial and magnetic properties.[163] Silver-cellulose nanocomposites were synthesized by microwave-assisted reduction of silver nitrate onto cellulose. The resulting nanocomposites exhibited high antimicrobial activity against both Gram-positive bacteria (*Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli*).[163] Iron oxide nanoparticles embedded into a sodium carboxymethyl cellulose matrix exhibited superparamagnetic-like behavior.[164]

Chitin and Chitosan

Chitin, the second most abundant biomaterial after cellulose, is found in the exo-skeletons of insects and crustaceans, making it the most abundant animal polysaccharide.[165] Chitin is also found in the cell walls of fungi and green algae, as well as in certain yeasts and protozoa.[166] Chitin is a biopolymer offering promising properties in a wide range of fields, including the biomedical, food, cosmetic, and textile industries, because of its biocompatibility, biodegradability, antimicrobial activity, and high tensile strength.[167,168,169] Chitin is a linear polysaccharide comprised of *N*-acetyl-glucosamine linked by $\beta(1{\rightarrow}4)$ glycosidic bonds, as shown in Figure 6. Commercial applications of chitin are limited by its solubility.[165] Chitin is only slightly soluble in highly polar solvents because of strong intermolecular hydrogen bonding. Chitin possesses high crystallinity and its melting temperature is above the temperature that triggers chemical degradation.[170]
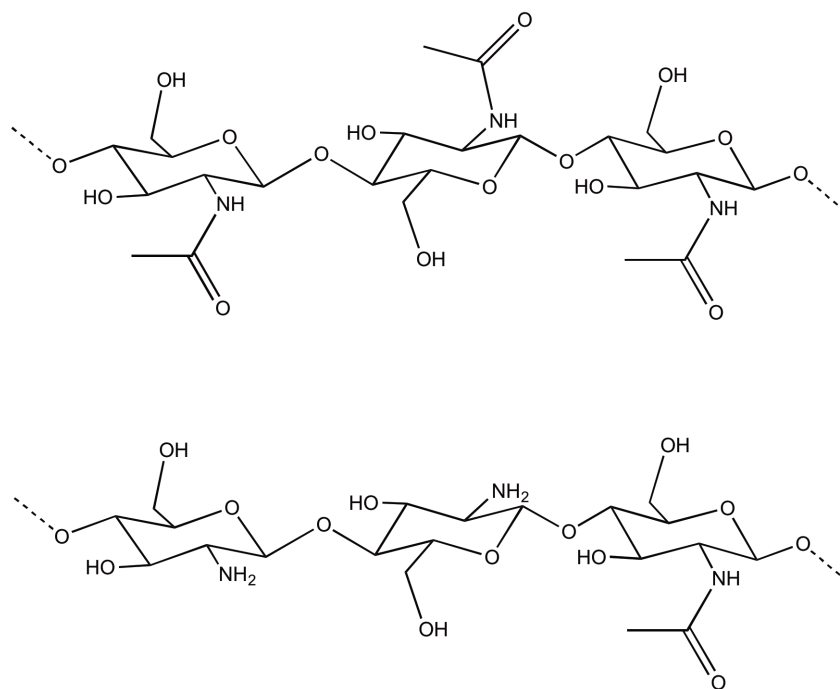

Figure 6. Structures of chitin (top) and chitosan (bottom).

Chitosan is a polysaccharide derived by the deacylation of chitin and consists of a random copolymer of *N*-acetyl-glucosamine and D-glucosamine, as shown in Figure 6. [171] The deacylation of chitin is typically carried out in alkaline medium, such as sodium hydroxide or potassium hydroxide, at high temperatures.[172] In practice, the complete deacylation of chitin cannot be achieved.[173] The degree of deacylation for chitosan can reach 90% under optimal conditions.[174,175] Excessive treatment conditions lead to depolymerization of the chitosan, rather than further deacylation.[176,177] Chitosan is soluble in mild acidic aqueous solutions and is more readily chemically modified than chitin.[178] Chitin has primary and secondary hydroxyl groups available for chemical modification, while chitosan has an amino group that can be chemically modified in addition to the hydroxyl groups.[179]

Chitosan has been used for a wide range of applications, such as paper finishing, textiles, food additives, insecticides, cosmetics, pharmaceutical, and biomedical applications.[180,181] Chitosan composites were used to make self-healing coatings that offer corrosion resistance, where the chitosan film acted as a reservoir of corrosion inhibitors underneath a protective top coating.[182] Chitosan films were reinforced with cellulose-containing fillers from wood pulp and sawdust.[183] Biopolymer membranes and composites were extensively investigated for their use as promising alternatives to conventional absorbent materials for water remediation by removing dyes, heavy metals, and other chemicals from wastewater.[184,185]

Of particular interest in chitin and chitosan is their use in biomedical applications because of their excellent physical properties, chemical stability, biocompatibility, biodegradability, and ability to be chemically modified.[186,187,188,189] Chitosan nanocomposites reinforced with calcium phosphate crystals were prepared for tissue engineering applications, because of their biocompatibility and strong adhesion to bone surfaces.[190] Rosmarinic acid biosensors for

pharmaceutical applications were developed by incorporating gold nanoparticles dispersed in ionic liquids into a chitin-based matrix synthesized by chemically crosslinking chitin with glyoxal and epichlorohydrin.[191] Chitosan nanoparticles and microparticles were used for delivery and controlled-release of drugs and nutrients, such as proteins and vitamins.[192,193,194]

Nanomaterials, such as nanofibers and nanocomposites, are another area of particular interest. Recently, biobased nanocomposites were made from cellulose nanocrystals[195] and nanofibers[196] with a chitosan polymer matrix. These materials exhibit good mechanical properties and water vapor barrier characteristics, which makes them suitable for applications in food packaging.[196] In fact, environmentally friendly, edible chitosan-cellulose nanofiber composite films[196] can be easily prepared when glycerol is used as a plasticizer.[197,198] Other nanocomposite systems recently investigated comprise chitosan nanocomposites with multi-walled carbon nanotubes synthesized by a simple solution evaporation method[199] and nanocomposites prepared from chitosan films and montmorillonite nanoclay particles, which were evaluated for biomedical and food packaging applications.[200,201]

b) Polylactic Acid (PLA)

Polylactic acid (*aka* polylactide) is one of the most widely used bio-based polymers on an industrial scale. Despite the misleading name, it consists of a polyester, resulting from the condensation polymerization of lactic acid (Figure 7A). Alternatively, polylactic acid can be obtained by ring-opening polymerization of lactide, a lactic acid dimer (Figure 7B). Polylactic acid has found many uses, ranging from every-day consumables to biomedical materials employed in cartilage repair.[202] Copolymers of PLA and polyglycolic acid have shown special promise as biomedical materials in early trials.[203]
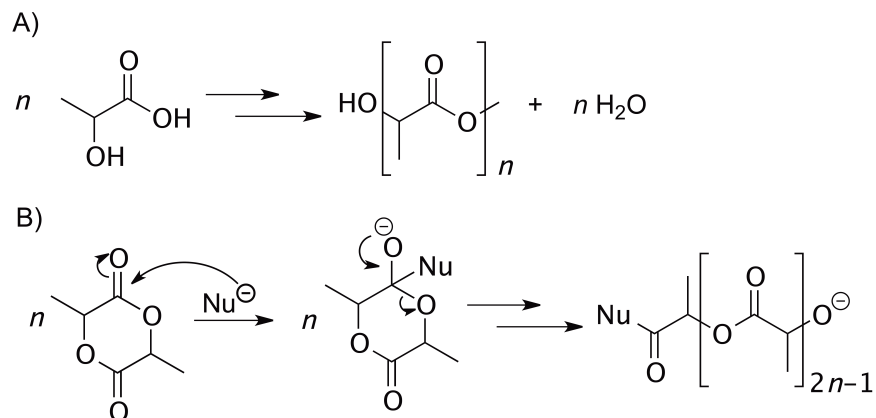
A)

B)

Figure 7. (A) Polymerization of lactic acid; (B) ring-opening polymerization of lactide.

Of particular interest are PLA composites reinforced with cellulose.[204] It has been demonstrated that the cellulose particles behave as nucleating agents, and therefore increase the cold crystallinity of the final composite.[204] As demonstrated in previous studies, the modification of cellulose is crucial in order to obtain significant improvements in mechanical properties.[205] It has also been shown that pure PLA is not biodegradable to a significant degree, and when blends of PLA, starch, and poly(hydroxyester-ether) are exposed to soil degradation conditions for one year, only the latter two components degrade significantly.[206] Advances in the processing of PLA/cellulose nanofiber composites were recently made by means of water dispersion of the fibers, followed by membrane filtration and compression molding. This process resulted in a significant increase in mechanical properties.[207] Table V summarizes the mechanical properties of the various PLA composites cited in this review.

Table V. Mechanical properties of select PLA composites.

Reinforcement (wt.%)	Modulus (GPa)	Strength (MPa)	Storage Modulus (GPa)	Elongation at Break (%)	Reference
-	3.6/tensile	49.6/tensile	6.4 at 50 ˚C	2.4	6
Microcrystalline cellulose (25)	5.0/tensile	36.2/tensile	10.4 at 50 ˚C	1.7	205
Wood flour (25)	6.3/tensile	45.2/tensile	13.1 at 50 ˚C	1.7	205
Wood pulp (25)	6.0/tensile	45.2/tensile	11.9 at 50 ˚C	1.9	205
Starch (20)	-	62.0/tensile	-	-	206
Cellulose nanofiber (32)	-	-	6.0 at 25 ˚C	1.4	207
Sisal fiber (30)	-	0.2/shear stress	-	-	208
Flax fiber (35)	1.9/tensile 2.1/flexural	37.9/tensile 25.0/fexural	-	2.3	211
Hemp fiber (30)	10.5/tensile 6.3/flexural	86.0/tensile 135.0/flexural 10.0/impact (J/m)	-	-	213
Wood fiber (30)	5.3/tensile 8.9/flexural	63.3/tensile 51.4/flexural 23.2/impact (J/m)	10.2 at 25 ˚C	-	215
Tricalcium phosphate (75)	6.0/tensile	80.0/bending	-	-	217
Glass fibers (single fiber)	80.0/tensile	450.0/tensile	-	-	220
Carbon nanotubes (7)	8.2/indenter	-	-	-	221

The reinforcement of PLA with natural fibers was extensively studied in the last decade. Sisal fiber was introduced in a PLA matrix, and it was shown that the rheological properties of the

29

resulting composites were directly affected by the fiber length, especially at lower fiber content.[208] In order to improve the interface adhesion between the matrix and the fibers, sisal fibers were pre-treated with NaOH and acetic acid. The process was used to introduce plasticity in the fibers and a series of mechanical tests revealed that the use of treated fibers as reinforcement resulted in an increase in mechanical properties.[209] Similarly, the pre-treatment of maple fibers was investigated for the preparation of PLA composites. It was demonstrated that the treatment conditions had an impact on the fiber integrity, which was reflected in the composite's final properties.[210] When flax fibers were used as reinforcement, the incorporation of amphiphilic additives helped to improve the interface adhesion between the fibers and the matrix, resulting in an increase in mechanical properties.[211] Also, the optimum fiber content was determined to be 35 vol.%.[212] PLA composites containing aligned, pre-treated hemp fibers exhibited a decrease in mechanical properties after exposure to hygrothermal aging conditions.[213] The optimum filler load was determined after compression molding of the PLA with pre-treated hemp fibers.[214] It was demonstrated that wood fibers imparted an overall increase in mechanical properties when added to PLA.[215] This trend was enhanced by the addition of maleated polypropylene as a coupling agent.[215] The addition of silane coupling agents to hybrid PLA/talc/wood flour hybrid composites also resulted in an increase in mechanical properties of the final material.[216]

Inorganic fillers were also used to reinforce PLA. A composite with mechanical properties similar to human cortical bone was prepared by ball milling β-tricalcium phosphate and adding it to PLA as reinforcement.[217] In another instance, bioactive ceramic calcium silicate was added to PLA and composites were prepared by three different processes: compression molding, spin coating, and film deposition.[218] These methodologies allowed for the preparation of bioactive

composites with CaSiO$_3$ loadings as low as 0.4 vol.%.[218] Significant increases in mechanical

properties were also observed when PLA was reinforced with 20-60 wt.% hydroxyapatite fibers

obtained from *ß*-calcium phosphate.[219] The use of glass fibers treated with PLA oligomers as

reinforcement in PLA composites was reported.[220] It was shown that this approach led to

composites with improved fiber-matrix adhesion.[220] Finally, PLA composites with good

mechanical properties were obtained after the dispersion of carbon nanotubes in the polymer

matrix.[221]

c) Polyhydroxyalkanoates (PHAs)

Similar to PLA, polyhydroxyalkanoates (PHAs) are polyesters derived from bio-based resources.

While PLA is obtained from plants, PHAs are produced and secreted by bacteria. The carbon

chain length of the repeating units in PHAs varies depending on the bacteria. It is striking that

after many years of extensive research activity on the topic, the production of PHAs at an

industrial scale is still not economically viable, and therefore it has not yet reached

commercialization.

Poly-3-hydroxybutyrate (P3HB) was the first PHA discovered and its chemical structure is

shown in Figure 8a.[222] The production of PHAs with specific molecular weights can be favored

by changes in the bacteria growth medium. As an example, polyhydroxyoctanoate (PHO) (Figure

8b) can be produced at higher yields when the bacterium *Pseudomonas oleovorans* is placed in a
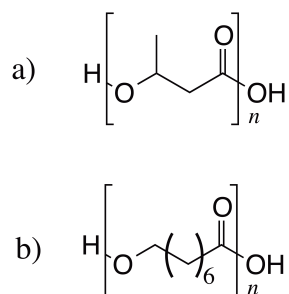
medium rich in diethylene glycol.[223]

a)

b)

Figure 8. Chemical structure of (a) poly-3-hydroxybutyrate (P3HB), and (b) polyhydroxyoctanoate (PHO).

PHAs have found wide use in the fabrication of inorganic composites for various biomedical applications. Hydroxyapatite, bioactive glass, and glass-ceramic fillers were added to PHA in order to confer improved mechanical properties for tissue engineering.[224] Besides their use in the biomedical field, PHA composites are of interest because of their biodegradability. A recent study showed that the biodegradability of P3HB and P3HB/valerate copolymers depends on the polymer's molecular weight, the technique used during processing, and its crystallinity.[225]

d) Proteins

The natural occurrence and preparation of protein composites was recently studies, where the polypeptide behaves like a matrix and minerals, such as calcium carbonate,[226] calcite,[227] and zinc oxide,[228] act as reinforcements. Composites with good mechanical properties were achieved with these systems. It was recently discovered that the addition of keratin to synthetic elastomers resulted in materials with good thermal and mechanical properties, decreased flammability, and enhanced resistance to thermo-oxidative aging.[229] Analogously, soy protein was added to a styrene-butadiene latex and the material's properties were compared to carbon black filled elastomers.[230]

Proteins isolated from soy were reinforced with coal,[231,232] jute,[233] clay,[234] and ramie fiber,[235] resulting in brittle materials. In a different application, the interaction of vegetable oils and proteins were investigated using peanut oil emulsions in a porcine myofibrillar protein matrix.[236] In that study, it was shown that protein-coated droplets of peanut oil were stabilized in water through disulfide crosslinking.

5) Conclusions

The technology developed over the last decade involving bio-based polymer composites is promising and research efforts in this area are expanding rapidly. Bio-based composites with a wide range of properties were prepared for various target applications. Naturally occurring polysaccharides were used both as the matrix and as reinforcements in the preparation of biocomposites. Polysaccharides were hydrolyzed, and the resulting sugars were modified and used as building blocks for the synthesis of novel matrix systems for biocomposite applications. One of the most popular bioplastics to date, PLA, served as the matrix for several bio-based composites. Similarly, there are numerous reports on the use of PHAs as the matrix in bio-based composite materials. Biocomposites from regular and modified plant oils were prepared by free radical, cationic, or ring-opening polymerization in the presence of various vinylic comonomers. These systems were reinforced with continuous glass fibers, functionalized organoclays, and a variety of natural fillers to afford biocomposites with high bio-based content. In many cases, the combination of a bio-based resin with a natural filler is not trivial, and requires major screening of synthesis parameters, including filler loading, until an optimum composite is obtained. In other instances, the resin composition is varied in order to show the versatility of a particular system, being able to tailor mechanical properties to the desired application. These are the main

reasons for such a broad range of bio-based content observed in the systems covered by this review.

Despite the great accomplishments in the development of bio-based materials to date, future research efforts in this area should include improvements in the current processes, examination of other naturally-occurring molecules or building blocks easily derived from them, exploration of other polymerization processes, and examination of these new materials in various industrial applications. As mentioned in the text, another area of great potential in the future is the reinforcement of vegetable oil-based polyurethane dispersion films with natural fibers in order to improve their overall properties. In the near future, it is expected that nano-composites from bio-based components become well established, and that structural and functional nano-materials see the light of day in successful commercial applications. As new incentives arise for the production and use of bio-based materials and biorenewable chemicals, it is expected, and needed, to carry out studies on the biodegradability/recyclability and life cycle analysis of the most successful bio-based systems.

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