

GELCLAD

Highly efficient cladding
eco-panels with improved
nano-insulation properties

DELIVERABLE D2.2

GELCLAD coupling agents
and additives

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ABSTRACT

This document provides details on coupling agents for functional WPCs products and their compatibility with different bio/polymers. The overall objective of this deliverable is to integrate information of the raw materials and their technologies to maximize their function for the GELCLAD materials to be produced.

INDEX

1	Summary.....	5
2	Introduction.....	6
3	Biodegradable polymers.....	9
3.1.	Cellulose-based polymers.....	10
3.2.	Starch based-polymers.....	11
3.3.	Lignin-based polymers.....	12
3.4.	Plant oil-based polymers.....	13
3.5.	Polyhydroxyalkanoates (PHA).....	13
3.6.	Poly(lactic) acid (PLA).....	17
4	Coupling agents.....	18
4.1.	Bio-based coupling agents.....	19
4.2.	Silanes.....	20
4.3.	Maleated coupling agents.....	21
4.4.	Isocyanates.....	23
4.5.	Triazine derivatives.....	24
5	WPC additives.....	26
6	Bio-based polymer composites.....	28
6.1.	Highlights of critical problems with bio-based polymer composites (ecoWPC)28	
7	Conclusions and future prospective.....	30
	References.....	31

1

SUMMARY

Bio-based polymer composites are in their infancy, there are success stories and promising developments, however, failures and substantial technological problems also exist. In order to draw fair conclusions and identify the directions for future research developments, this document present fundamental knowledge about biopolymers, coupling agents and different added-value additives resulting in bio-composites. In bio-based polymer composites, coupling agents and additives are used extensively to improve their overall performance. Additionally, some critical issues with bio-based polymer composites and suggestions for future work are discussed, emphasising the roles of material scientists, textile engineers and processing machinery technologist for future of innovative bio-based polymer composites and their effective utilisation for GELCLAD products.

2

INTRODUCTION

The global production capacity of bio-based polymers and bio-composites has demonstrated a dynamic growth [1-3]. With increasing oil prices, conventional polymers are becoming rapidly expensive, moreover due to environmental concerns and market trends, the bio-based polymers and bioplastics have attracted many research efforts [3-11]. The development of biodegradable polymer as an alternative to petrochemical counterparts is an important waste management strategy.

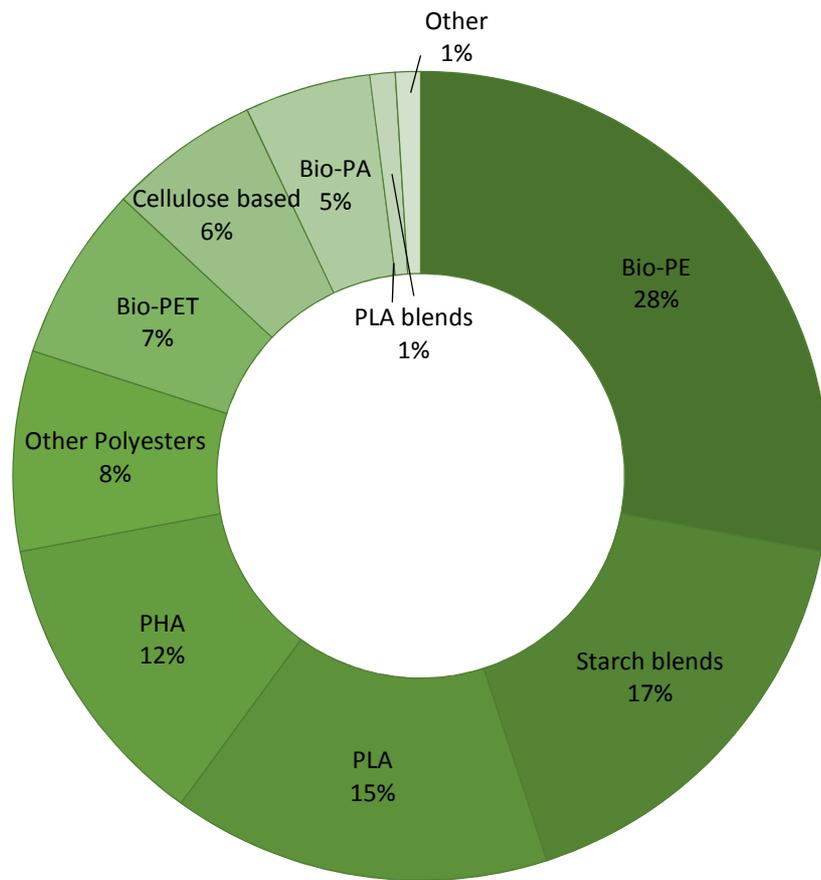


Figure 1: Worldwide biopolymer production capacities in 2010 according to polymer type [3]

Fig. 1 illustrates the worldwide bio-based polymer production capacities according to polymer type [3]. It is evident that starch and its blends, Poly(lactic acid) (PLA) and several types of polyhydroxyalkanoates (PHAs) have highest significance amongst bio-based polymers. On the other hand, the productions of conventional polymers such as polyethylene (PE) or polyethylene terephthalate (PET) based on renewable resources are also gaining ever more significance [3]. Regarding bioplastics, it is reported that in 2014, the global production capacities amounted to 1.7 million tonnes. This translates to approximately 0.68 million hectares of land, as depicted in Fig. 2. Therefore, the surface required to grow sufficient feedstock for

bioplastics production is calculated to be around 0.01% of the global agricultural area of a total of 5 billion hectares. Assuming constant growth of the bioplastics market based on the current stage of technological development, a market of 7.8 million tonnes could be realised by the year 2019, translating to about 1.6 million hectares, or around 0.02% of the global agricultural area. This estimation however, does not include the expected increased share of food residues, non-food crops or cellulosic biomass, which could lead to a smaller land use demand for bioplastics than the predicted amount aforementioned [1].

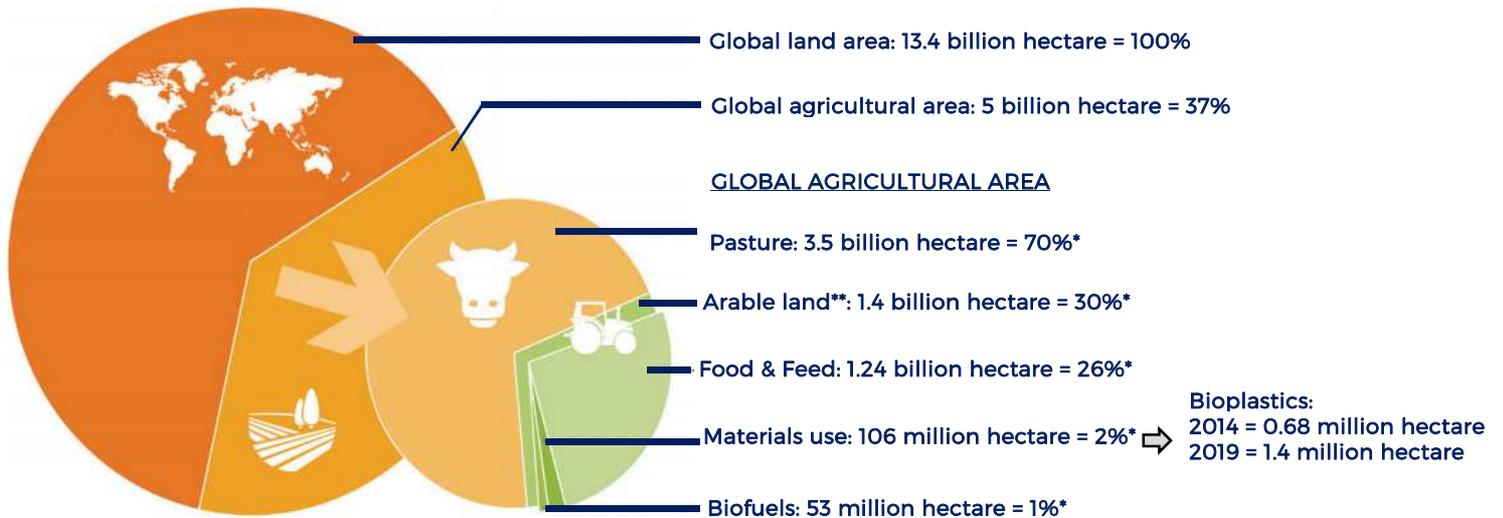


Figure 2: land use for bioplastics in 2014 and 2019 [1]. *In relation to global agricultural area **Also includes approximately 1% fallow land

Biopolymers have seen a tremendous increase in use as a matrix for natural fibre reinforced composites. Bio-based polymer composites could have great potential being implemented in construction industry as well as automotive. The modern construction sector is undertaking a period of dramatic policy swing and priority alteration from a profit-charged business mechanism to a socioeconomic and environmentally driven sector. The environmental impact of the construction industry has been the subject of much scrutiny. Energy consumption in the use and the construction of buildings accounts for about 40% of all CO₂ emissions, 15% of which could be attributed to the production of construction materials [2, 3].

The different components of polymer composites make the reuse and recycling challenging, where it is frequently preferred to perform the direct disposal in a dump, or incineration [4, 5]. This, has inspired the scientists to research on new alternatives, able to replace petrochemical polymer composites with substitutes having lower environmental impact, higher biodegradability and thus often referred to as bio and/or green composites [4, 6].

Polymer composites filled with natural organic fillers, such as wood plastic composite, where the composite is utilising a polymer as a matrix and cellulose/sawdust material as filler, has gained great interest in recent years due to its wood like appearance, lower manufacturing cost, and most importantly, its environmental friendly properties [7-10]. However, the

incorporation of hydrophilic natural fibres in polymer leads to heterogeneous system whose properties are inferior due to lack of robust adhesion between fibres and polymer matrix. The treatment of fibres for improved adhesion is a critical step in the development of such composites. This could be bleaching, grafting of monomers, acetylation, and so on. In addition to the surface treatment of fibres, use of a coupling agent and/or additive for stress transfer across the interface could also be effective. The coupling agent could be a polymer with functional groups grafted onto its chain [11].

Natural fibres and polymers interaction, i.e. interfacial bonding, remains as one of the main technical problems delaying the successful commercialisation of bio-based polymer composites. Melt rheological characteristics are also essential to understand the behaviour of the processing of a polymer matrix and provide fundamental information on the effect of fibre/filler, coupling agent, and compounding methods on melt-state viscoelastic properties [12].

In this deliverable, we attempt to deliver a sensible overview of recent scientific trends and achievements in the field of biodegradable polymers and coupling agents, leading to bio-based polymer composites and elucidation of their interfacial mechanism. Clear and feasible strategies to overcome the associated problems with bio-based polymer composites are proposed along with directions for further research.

3

BIODEGRADABLE POLYMERS

Cellulose, hemicelluloses, lignin, silk and starch are typical examples of natural polymers which exist in nature as macromolecules. There is additional category of materials which consists of the natural-based or bio-based synthetic polymers, the monomers of which are derived from renewable resources. PLA as well as bio-based conventional polymers like PE, PET and polyamide (PA) belong to this category, additionally bacterial polyesters can be considered both natural and natural based materials, since the polymer is produced by bacterial fermentation in an industrial process [13]. The concept of biodegradability is independent of the categories aforementioned, meaning that biodegradable polymers may not necessarily be of natural origin. The conditions for the determination of the bio-based content of polymeric materials are described in the European standard CEN/TS 16295:2012 [13]. This method is based on the amount of bio-based carbon as a fraction of the total organic carbon content. However, legislative details and exact protocols for the biodegradability categorisation need to be elaborated in more details. Biodegradation could be defined as the degradation of a polymer in natural environments, which includes changes in chemical structure, loss of mechanical and structural properties, and eventually, changing into other compounds like water, carbon dioxide, minerals, and intermediate products like biomass and humic substances [14]. The natural environments contain chemical, biological, and physical forces with imposing factors like temperature, humidity, pH, oxygen presence, and so on, which regulate the rate and products of the biodegradation process [15].

Polymer science is facing new challenges and opportunities, instead of the development of novel polymeric materials and new polymerisation routes, blending could represent a relatively cheaper and faster technique to tailor the properties of biopolymer and/or bioplastics [16]. Blending, for instance could improve the impact resistance of brittle polymers, although, this requires detail investigation on the miscibility, structure and property relationships. This approach could be crucial in increasing the competitiveness of biopolymers. The chemical structure of biopolymers opens up possibilities to their reactive modification. Copolymerisation, grafting, trans-esterification, and the use of reactive coupling agents have all been utilised with success to achieve polymers and blends with improved properties [13].

The use of biodegradable polymers as bulk commodity materials are limited to scarce applications because of the strong cost-competition with cheaper petroleum-based polymers, and their insufficient thermo-mechanical properties [17, 18]. Inexpensive and easy process to manufacture biodegradable polymers is extremely necessary for their commercial viability and successful scale-up.

3.1. Cellulose-based polymers

There is a significant potential in the production of polymers from cellulose derived monomers [19, 20]. Cellulose is the most abundant natural biopolymer, a linear homo-polysaccharide composed of β -D-glucopyranose units connected by β -1-4-linkages with a repeating unit of cellobiose [21]. Cellulose is a highly crystalline, high molecular weight polymer, which is infusible in all but the most aggressive hydrogen bond-breaking solvents such as N-methylmorpholine-N-oxide. Because of its infusibility, cellulose is usually converted into derivatives to permit easier processing. Such derivatives include cellulose ethers, for example methylcellulose (MC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose (HPMC), and cellulose esters, such as cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB). Between the cellulose ethers, HPC is a true thermoplastic resin and is, therefore, capable of being extruded into films from the molten state [22]. Nanocomposites from CA and organically modified clay were prepared by Park et al. [23], for plasticising CA, they used triethylene citrate as an eco-friendly plasticiser instead of toxic phthalate plasticiser.

Sawai et al. [24], developed cellulose-based polymer with good melt-processability. They studied the molecular size, functional groups and the degree of substitution on the mechanical and thermal properties of cellulose-based polymer, where it was shown that plasticity improved with the size and number of added substituents, and the balance between mechanical performance and plasticity was enhanced through the combinational use of small and large molecules added to side chains. Additionally, the impact strength of cellulose-based polymer was increased by the addition of ether/ester groups together. Interestingly, injection moulding of this material was carried out, where good rheological and processing characteristics were observed [24].

The implementation of cellulose into GELCLAD products will mainly result in lower densities while the degree of reinforcement will mainly depend on the aspect ratio of the cellulose. The implementation of nanofiber cellulose as nanofiller for the GELCLAD products can enhance the tensile strength as well as contribute to the flexural strength; however the down side can be the vulnerability of cellulose to moisture which will have to be addressed by crosslinking or surface modification which can affect the final biodegradability.

3.2. Starch based-polymers

Starch is mainly composed of two homopolymer of D-glucose, i) amylose, a mostly linear α -D(1, 4')-glucan and ii) branched amylopectin, having the same backbone structure as amylose but with many α -1, 6'-linked branch points [25]. Starch is also an abundant biopolymer which could be derived from renewable resources such as corn, potato, wheat, and etc. starch occurs as granules in plant tissue from which it could be recovered in large quantities [26]. Two main features of starch make it unique and versatile material. First, is its biodegradability, i.e. it degrades into sugars and organic acids that serve as feedstocks for producing industrial chemical, thermoplastics, and biofuels. Second, due to its chemical structure, starch polymer is amenable to a selection of chemical and enzymatic modifications that enables the synthesis of novel functionalities in starch polymer [26]. Starch is not truly thermoplastic in nature. However, it could be converted into a continuous polymeric entangled phase by mixing with enough aqueous or non-aqueous plasticisers, i.e. polyols such as glycerol [27]. Plasticised starch based films cannot meet all the requirements of packaging application. They are water sensitive and lose their barrier properties upon hydration [28, 29]. Additionally, retrogradation and crystallisation of the mobile starch chains affect thermomechanical properties. Although, the mechanical performance of these materials for packaging application could be easily enhanced by incorporation of a synthetic polymer and/or organic reinforcing fillers [30-32]. In order to produce a completely biodegradable plastic derived from natural renewable resources, great efforts have been made to blend PLA and starch. Blending starch and PLA could dramatically reduce the cost and enhance the biodegradability of blends [33-36]. Starch rheology is not always suitable for the use as a matrix in composites, especially for their high sensitivity to creep and scattering of properties [37]. Some strategies have been proposed, one is blending with nano-metric form of clay. Results suggested that during gelatinisation, the structural part of starch (i.e. amylose), interacted with a nano-clay interlayer and so enhanced reinforcement and modulus values. This was mainly effective with wheat and corn starch, and less so with potato and waxy corn, since the latter had modulus values rapidly decreasing at higher temperatures [38].

The processing properties of starch-based polymers are much more complex than conventional polymers. The processing (especially extrusion) of starch-based polymers involves multiple chemical and physical reactions, e.g. water diffusion, granule expansion, gelatinisation, decomposition, melting and crystallisation. Due to the multiphase transitions of starch, the microstructures and mechanical properties of starch-based materials strongly depend on the processing techniques and conditions [39].

Starch is completely biodegradable and is an environmental friendly material and is very easily available and has a relatively low cost. One of its major drawbacks is its rapid disintegration when in contact with water or high moisture content and has relatively poor mechanical properties compared to other biodegradable polymers the can be used for the GELCLAD products . However for it to be implemented into GELCLDA products it can be blended with other biopolymers or thermoplastic to create a more biodegradable GELCLAD product such as blending PVC and Starch together.

3.3. Lignin-based polymers

After cellulose, lignin is the second most abundant natural biopolymer. Lignin is an extremely complex three-dimensional polymer formed by radical coupling polymerisation of *p*-hydroxycinnamyl, coniferyl and sinapyl alcohols. These three lignin precursors monolignols give rise to the so called *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) phenylpropanoid units, which show different abundances in lignin from different groups of vascular plants, as well as in different plant tissues and cell wall layers [40, 41]. These aromatic building units are linked with a variety of ether and carbon-carbon bonds. The predominant linkage is the so called β -O-4 linkage. Lignin is a by-product of cellulose in the paper pulp production, and has rather low added-value applications. However, changes in the paper market have inspired focus on other applications for lignin. Furthermore, the emergence of bio-refinery projects to develop biofuels, bio-based materials and chemicals from carbohydrate polymers should also generate large amounts of lignin with the potential for value addition. These developments have brought about renewed interest in the last decade for lignin and its potential use in polymer materials [42, 43]. Lignin polymer presents a few hurdles that require further investigations to expose its full potential [44].

High-volume lignin application could be plant-derived plastics and composites. The synthesis of engineering plastics and thermoplastic elastomers, polymeric foams, and membranes from lignin with comparable properties to those from petroleum products has been reported [45]. Many different strategies of filler/polymer compatibilisation have been considered for improvement of reinforcing effect of lignin as filler [46]. These include: the use of lignin-grafted polymers (lignin/polystyrene (PS) blends) [47], surface grafting of lignin particles (lignin/ PE blends) [48], use of plasticisers to decrease the degree of association of lignin (lignin polyvinyl chloride (PVC) blends) [49], or decrease in the lignin polarity by grafting ethyl or acetyl groups on hydroxyls (lignin/hydroxypropylcellulose blends) [50].

Lignin is also the most abundant source of renewable phenolic groups. It has long been considered as potential replacement of phenol in thermoset resins, such as phenol formaldehyde (PF) resins, already addressed in different reviews [51, 52]. PF resins are formed by the reaction of formaldehyde on ortho and para positions of phenol, resulting in a crosslinked, three dimensional networks, often used as adhesive.

Future development of green lignin-based polymers depends on novel processing technologies along with tailor made biomass containing lignin with desired chemical and physical properties for a host of lignin-based material applications.

Lignin is produced as a by-product of the paper/pulp industry and can be produced in high volumes allowing for continuous production. Waste lignin from industries offers a number of advantages, such as sufficient reactive functional groups, film-forming ability, high carbon content, compatibility with diverse industrial chemicals, good stability good rheological and viscoelastic properties. Thus lignin can be an ideal candidate for GELCLAD however the main disadvantage is its high brittleness which can be problematic due the intended applications of the GELCLAD products that require high impact strengths .

3.4. Plant oil-based polymers

Plant oils constitute a rich source for many different polymers and polymer precursors. Although, the role of oil-based products may seem modest in some cases (partial replacement of synthetic materials), there is a clear trend to increase the percentage in materials for the formulations of polymers/composites with higher value added applications [53]. Plant oil derived polymers are being used in numerous applications including paints and coatings, adhesives, and biomedicine [54]. Plant and/or vegetable oils represent a renewable resource that can be used as starting raw material to synthesise new products with a wide selection of structural and functional variations. The abundant availability and the relatively low cost, make plant oils an industrially striking raw material for the polymer and/or plastic sectors. Naturally occurring plant oils and fatty acids derived thereof, are considered to be the most important renewable feedstock processed in the chemical industry and in the preparation of bio-based functional polymeric materials [55–59]. While numerous synthetic approaches have been implemented, more recent examples are pointing in the direction of catalytic transformations and other efficient reactions to achieve a more sustainable production of polymers from plant oils [58]. Some of the plant oil-based polymers and precursors are currently commercially viable and there are companies that offer derived bio-based polymers (epoxy, alkydic and polyurethanes precursors) for specific applications. Plant oils have been extensively used for the production of polymer composites incorporating organic or inorganic particles or fibres, both synthetic and natural, with micro- and/or nano- size [53, 60–62]

Güner et al. [55] comprehensively reviews the structure, property and modification of triglyceride oils and the synthesis of polymers from there. Polymers from triglyceride oils are prepared via conceptually different strategies. Various polymerisation methods, including condensation, radical, cationic and metathesis procedures have been applied. Triglycerides are highly functionalised molecules and they have been utilised in the synthesis of cross-linked polymers by two main approaches. The first one takes advantage of the naturally occurring functional groups present in triglycerides, such as internal double bonds, alcohols, or epoxides, which can be polymerised through various methods. The second approach relies on chemical modifications prior to polymerisation. This strategy tackles the drawback of the low reactivity of natural triglycerides, which usually only contain double bonds, by the introduction of easily polymerising functional groups, which subsequently, extends the synthesis possibilities. The hydrolysis of triglycerides provides glycerol and a mixture of fatty acids [58]. Fatty acids have been used for a long time by polymer scientists for the development of polymeric structures, both directly and as building blocks for the synthesis of more sophisticated monomers [59].

One of the most common oil based polymers are soya flour based which can target useful desirable properties of the GELCLAD products such as high impact resistance, good barrier properties, low dielectric constant with low expansion coefficients. Soya flour from literature showed excellent bonding with wood where it has been used to produce particle boards without the use of thermoplastic resin. However as oil derived polymers are still an emerging field most applications present a partial replacement of synthetic polymers/resin to introduce “green” materials in the formulation which can be the case for GELCLAD.

3.5. Polyhydroxyalkanoates (PHA)

PHAs are biodegradable polymers that can be produced by many different types of microorganisms, i.e. bacteria, from a renewable source. In comparison to conventional synthetic polymers, PHA has noticeable ecological advantages since they are nontoxic [63, 64], and 100% bio-based which is biodegradable even in cold sea water [65]. PHAs can be completely bio-degraded within a year by a variety of microorganisms. This biodegradation results in carbon dioxide and water, which return to the environment [66]. Promising strategies involve genetic engineering of microorganisms and plants to introduce production pathways. This challenge requires the expression of several genes along with optimisation of PHA synthesis in the host. Although, excellent progress has been made in recombinant hosts, the barriers to obtaining high quantities of PHA at low cost still remain to be solved. The commercially viable production of PHA in crops, however, appears to be a realistic goal for the future [66].

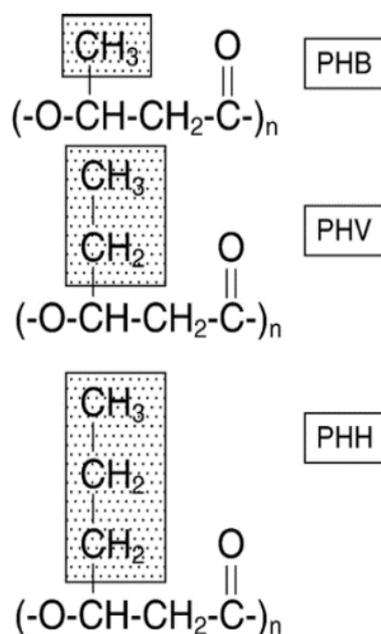


Figure 3: chemical structure of PHAs; the pendant R groups (shaded boxes) differ in chain length from one carbon (C1) to over 14 carbons (C14). Structures shown here are polyhydroxybutyrate (PHB) (R=methyl), polyhydroxyvalerate (PHV) (R=ethyl), and polyhydroxyhexanoate (PHH) (R=propyl) [66].

PHAs are composed of 3-hydroxy fatty acid monomers, which form linear, head-to-tail polyester shown in Fig. 3. PHA is typically produced as a polymer of 10^3 to 10^4 monomers, which accumulate as inclusions of 0.2-0.5 μm in diameter. These inclusions or granules are synthesised and stored by both gram positive and gram negative bacteria without hazardous effects to the hosts. PHA, which includes polyhydroxybutyrate (PHB) homopolymers, polyhydroxybutyrate-co-hydroxyvalerate copolymers (PHB/V) and other related linear polyesters, could have significant opportunities for marketability. Different sources (i.e. natural isolates, recombinant bacteria, plants) and methods are being investigated to exert more control over the quality, quantity and economics of poly(3-hydroxybutyrate) (PHB) production [67]. PHB marketing potential is restricted by some flaws such as brittle nature and melting temperature close to degradation phase, which restricts the processing window [68].

Although, PHAs have advantages over the conventional plastics, widespread application of PHAs is hampered by high production cost [69]. The selections of suitable bacterial strains, inexpensive carbon sources, efficient fermentation and recovery processes are important aspects that should be taken into consideration for the commercialisation of PHA. The price and the current possible yields of PHAs hinder its competitiveness with the cheap, petrochemical plastics. In economic analyses it is shown that the carbon source, e.g. glucose, contributes almost 30% to the overall cost of PHA in engineered *Escherichia coli* [70]. Therefore, cheap carbon sources would significantly lower the final price and increase the availability of this bioplastic. The cost of producing the PHA via syngas fermentation is less expensive than producing PHA by sugar fermentation, which ranged from 4 to 6 US\$/kilogram [71].

PHA production from mixed cultures and renewable organic wastes as a carbon source [72, 73] is also striking due to the decrease in the production cost of the process [74]. Commercialisation of plant derived PHA would require the establishment of transgenic crop plants (i.e. straw biomass) that in addition to high product yields have normal plant phenotypes and transgenes which could be stable over several generations [75]. Production of PHA on an agronomic scale would enable the synthesis of biodegradable plastics in the million tonne scale compared to fermentation, which produces material in the thousand tonne scale. PHA could potentially be produced at a cost of 0.20 to 0.50 US\$/kilogram if they would be synthesised in plants to a level of 20 to 40% dry weight, this could then be competitive with the petroleum based plastics [67].

For industrial production of PHA, it is desirable to develop strains that can reach high final cell density in a relatively short period of time and produce high PHA content [76]. The production of PHAs can be undertaken using various materials including sugar-based, starch-based, whey-based, and glycerol-based media as shown in Table 1. The statistics presented in Table 1 illustrates that starch and whey-based materials are easily utilised by microorganisms, as shown by their much higher production levels [68].

Table 1: some of PHA production examples from various sources and media types

Microorganism	Carbon source	Production (g/L)	level	Ref.
<i>Azotobacter vinelandii</i>	Molasses	23		[77]
<i>Pseudomonas fluorescens</i>	Molasses	22		[78]
<i>Ralstonia eutropha</i>	Potato starch	94		[79]
<i>Cupriavidus necator</i>	Glycerol	38		[80]
<i>Cupriavidus necator</i>	Glycerol	16		[81]
<i>Escherichia coli</i>	Whey	96.2		[82]
<i>Bacillus megaterium</i>	Sugarcane molasses	1.27		[83]

Alkanoates in their different forms and classes are eco-friendly and biodegradable and has been reviewed to prepare WPCs with reported properties to that prepared with thermoplastic polymers. The downside of implementing PHB into GELCLAD products is current high costs factors associated with the production of PHA.

3.6. Poly(lactic) acid (PLA)

PLA is a biodegradable and compostable thermoplastic derived from renewable plant sources, such as starch and sugar. Corn, the common source of biomass, is the most effective source for providing high-purity PLA [20]. PLA is aliphatic polyester made up of lactic acid (2-hydroxy propionic acid) building blocks [84]. In the framework of environmentally friendly processes and products, PLA is considered the most effective biopolymer for bio-based composites [20]. Traditionally, the uses of PLA have been mainly limited to biomedical areas due to its bio-absorbable characteristics. Over the past decade, the discovery of new polymerisation routes that allow the economical production of high molecular weight PLA, have led in an increased interest in use of PLA for consumer goods and packaging applications [84]. The first attempt to prepare PLA was ascribed to Pelouze in 1845 by condensing l-lactic acid and removing water continuously, leading to low molecular weight PLA [85]. However, due to its reversibility, this poly-condensation method suffers from several problems including the need of high temperature, continuous removal of by products (most often water) and long reaction times. Therefore, ring-opening polymerisation of lactide (cyclic dimer of lactic acid) promoted by protic compounds (i.e. water, alcohol and amine) as initiators and tin(II) octoate ($\text{Sn}(\text{Oct})_2$) as catalyst, is industrially favoured to achieve high molecular weight PLA in bulk (absence of solvent) [86]. In previous years, the most negative point of PLA was its price in comparison with petrochemical-based polymers. However, innovative ideas to reduce PLA final price and more eco-friendly manufacture processes, could include, i) utilisation of crop residue (stems, straw, husks, and leaves) from biomass crops (i.e. wheat straw), ii) utilisation of un-fermentable residues for the heat source, and iii) substituting some part of electricity energy by wind power energy. These approaches decrease the consumption of fossil fuels and corn starch as raw materials and also diminish polluting air, water, and waste emissions to the environment [14]. The present PLA price is much lower than in previous years, but it is not fixed and it could even be lower in the near future.

The implementation of PLA into the GELCLAD products can significantly enhance the strength and modulus however the main disadvantages may include low resistance to conditions of high heat and humidity, low heat distortion temperature (HDT), low flexibility. In order to overcome durability issues associated with moisture crosslinkers can be introduced however this may come at a cost of the biodegradability of the GELCLAD products.

4

COUPLING AGENTS

In previous section we summarised biopolymers, but in order to fully realise the potential of biopolymers in bio-based composites, coupling agents must be introduced. Coupling agents form chemical and/or physical bonds between fibre and polymer matrix phases to promote interfacial bonding in composites. They facilitate the functional groups, in specific hydroxyl groups, at one end to react with the fibre surface and another functional group at the other end of bond with the polymer matrix [87, 88]. The understanding of coupling agent structure and their mechanisms is essential for designing an optimised interface between the biopolymers and natural fibres/fillers, resulting in high quality bio-based polymer composites. This could lead to their dissemination into new markets for construction and automotive. The mechanism of coupling agent is illustrated in Fig. 4. The coupling agent is chemically bonded with the hydrophilic fibres and blended by wetting in the polymer chain [89].

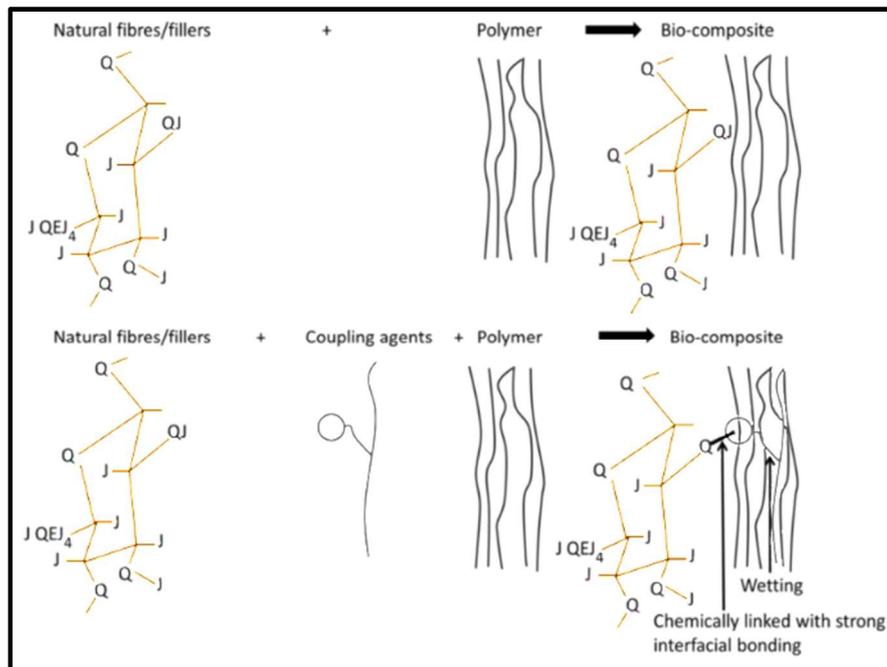


Figure 4: mechanisms of coupling agent compatibilisation between hydrophilic fibre/filler and hydrophobic polymer matrix

4.1. BIO-based COUPLING AGENTS

Undoubtedly, with increased environmental awareness, it seems valuable if coupling agents used in bio-based polymer composites were non-toxic and biodegradable to preserve the renewability and biodegradability characteristics. It is vital therefore, to have a bio-based coupling agent which enables the production of a fully biodegradable polymer composite without emitting toxic compounds. Biopolymers, such as chitin, chitosan and zein, have been used as coupling agents in bio-based polymer composites. Zein is a natural protein extracted from corn, which has many functional groups on its molecular chain that can act as coupling agents for bio-based polymer composites. Zein possesses polar groups such as carboxyl and amino groups which could react with the hydroxyl group of fibres via hydrogen bonds. Moreover, the alkyl and aryl groups can react with a polymer matrix through hydrophobic interactions [90]. It was shown that zein could enhance the storage moduli of flax-polypropylene composites [91, 92]. Zein was also used as coupling agent in kenaf-polypropylene composite, where, it was found to improve the mechanical and viscoelastic properties [90]. Alternatively, chitin and chitosan, which are natural polysaccharide polymers of N-acetyl glucosamine and glucosamine, respectively, have been used as coupling agents, to improve the mechanical properties of wood flour-PVC composites [7]. The stronger interfacial adhesion was attributed to the acid-base interaction between the chlorine atoms of PVC and the amino groups of chitin and chitosan on the wood flour surface [7]. The advantages of chitin and chitosan are their wide availability, non-toxicity, biocompatibility and lower cost compared with many synthetic coupling agents.

Corrales et al. [93], used a fatty acid derivate (oleoyl chloride) as coupling agent to confer hydrophobicity and resistance to jute fibres. This reaction was applied in swelling and non-swelling solvents, pyridine and dichloromethane, respectively. Oleoyl chloride reacted with cellulosic hydroxyl groups by an esterification reaction to form ester functionality. Esterification was however, limited to the hydroxyl groups on the external surface of the fibres. The long hydrocarbon chain of oleoyl chloride made the fibre surface hydrophobic and thus compatible with the polymer matrix [93].

Effects of lysine-based diisocyanate (LDI) as a bio-based coupling agent on the properties of bio-composite from PLA, poly (butylene succinate) (PBS) and bamboo fibre (BF) were investigated by Lee and Wang [94]. It was found that tensile properties, water resistance, and interfacial adhesion of both PLA/BF and PBS/BF composites were improved by the addition of LDI, whereas thermal flow became somewhat difficult due to crosslinking between polymer matrix and BF.

The main factor and benefit of implementing Biodegradable coupling agent is to maintain to synthesize fully biodegradable GELCLAD products without emitting toxic or noxious components .

4.2. SILANES

Silanes could form chemical links between fibre surface and a polymer matrix, by using their bifunctional structures. Silane chemical structure could be represented as R-Si-X₃, where R is a functional organic group and X is a hydrolysable group that forms silanols in the presence of moisture [87, 88]. Silanols and hydroxyl groups of natural fibres could then form covalent bonds of -Si-O-C [95-97]. Table 2 presents several silanes that have been used as coupling agents in composites. The functionality of the R group plays a major role in the reactivity of silane towards polymer matrix. Alkyl groups are designed to form optimum compatibility with the hydrocarbons backbones of matrices. Vinyl, amino, mercapto, and methacryl groups are capable of forming covalent bonds with the reactive groups of a polymer matrix [98].

A variety of silanes, frequently trialkoxysilanes have been applied as coupling agents in the bio-based polymer composites to endorse interfacial adhesion and increase the properties of composites. Xie et al. [87] summarises recent progress in using silane coupling agents for natural fibre reinforced polymer composites, and explains the interaction mechanisms between natural fibres and polymer matrices. The effects of silane treatments on the mechanical and physical performance of the resulting composites are also presented [87]. Silanes have been successfully applied in inorganic filler reinforced polymer composites such as glass fibre reinforced polymer composites, e.g. [99] and mineral filled polymer composites, e.g. [100, 101]. Physical blending of the silane-treated fibres and the thermoplastic matrices improves their mutual adherence through inter-molecular entanglement, or acid-base interactions [87].

Table 1: chemical structure of silanes and their polymer matrices

Name	R	X	Matrix	Ref.
Hexadecyltrimethoxy silane	-(CH ₂) ₁₅ CH ₃	-OCH ₃	Epoxy, Polyethylene, Natural rubber.	[96, 102]
Vinyltrimethoxy silane	-CH = CH ₂	-OCH ₂	Polyethylene.	[103]
Vinyltri(2-methoxy ethoxy) silane	-CH = CH ₂	-OCH ₂ CH ₂ - OCH ₃	Polyethylene, Polystyrene.	[104, 105]
γ-Aminopropyl triethoxy silane	-(CH ₂) ₃ NH ₂	OCH ₂ CH ₃	Polyethylene, Poly (lactic acid), Epoxy.	[106-108]
γ-Mercaptopropyl trimethoxy silane	-(CH ₂) ₃ SH	-OCH ₃	Polyethylene, Epoxy, PMMA, Natural rubber.	[96, 102]
γ-Methacryloxypropyl trimethoxy silane	-(CH ₂) ₃ -O-C-C(=O) CH ₃	-OCH ₃	Polyethylene, Polystyrene, PMMA, Natural rubber.	[96, 102, 104]

Aminosilanes, especially γ -aminopropyltriethoxysilane (APS), are most extensively reported in the literature as coupling agents between natural fibres and thermoplastics or thermosets [87]. Vinyl- and acryl-silanes are coupling agents that form covalent bonds with polymeric matrices in the presence of peroxide initiators. On the other hand, methacrylate-functional silanes could show high levels of reactivity with unsaturated polyester

matrices [104], whereas azidosilanes could effectively couple inorganic fillers with thermoplastic matrices [109, 110].

The interaction mechanism between the silane-treated fibre and the polymer matrix is a crucial factor for the mechanical properties of the resulting bio-based polymer composites. There are several different means reported to apply silanes to natural fibres. These can be divided into fibre surface treatment and cell wall modification. Spraying is a relatively easy way to treat the fibre surface with a silane solution. Although, this only results in a surface coating and the inside of cell walls is left untreated. In a processing method [111], silane solution and initiator were directly pumped into an extruder during extrusion process of natural fibres and thermoplastic matrices. The extruded composites were then exposed to an environment with high humidity (100%) and temperature (90°C) in order to complete the hydrolysis and condensation processes of the silane. This technique takes a long time at the hydrolysis and condensation stage. In addition, the silanes added will not only be distributed on the interface of fibre and matrices, but some also in the matrices, which could lead to waste of the silanes. On the other hand, for impregnation process, it is considered that the penetration of silanes into cell walls is influenced by the molecular size of silane which is subsequently influenced by the aging of the hydrolysed silane solution. Improper hydrolysis processes may result in a fast condensation of silanols, thereby, prematurely increasing the molecular size of the silanes. In this case diffusion of silanes into the cell walls will be limited. The bulking treatment of fibre cell walls can change its properties, and as a result promote the performance improvement of the resultant composites. In comparison to the surface treatment, i.e. spraying, the impregnation process could cause problems for fine and short fibres/fillers, as they may aggregate and therefore, not be evenly dispersed in the solution [87].

Silane can help during the processing of GELCLAD products for lowering the viscosities during compounding and can enhance the flexibility and result in smoother surfaces of the final GELCLAD products the main disadvantage can be associated with handling a safety silane

4.3. MALEATED COUPLING AGENTS

Maleated coupling agents are widely used to strengthen bio-based polymer composites. The established role of maleated coupling agents is the effective interaction of maleic anhydride with the functional surface of fibres [112]. Maleated coupling agents are made by grafting maleic anhydrides onto polymers to form copolymers such as maleated polyethylene (MAPE), maleated polypropylene (MAPP), and maleated polystyrene (MAPS). During grafting, the anhydride groups of maleated copolymers could react with hydroxyl groups of natural fibres via esterification. Schematic in Fig. 5 represents chemical reaction for the natural fibre coating with maleated copolymer [98]. It has been shown that, a similar property between the polymer matrix and the treated fibre enables a better entanglement interlock at the interface [113, 114]. The improvement of strength performance of bio-based polymer composites with the addition of MAPP was reported for various natural fibre-PP composites [11, 115, 116].

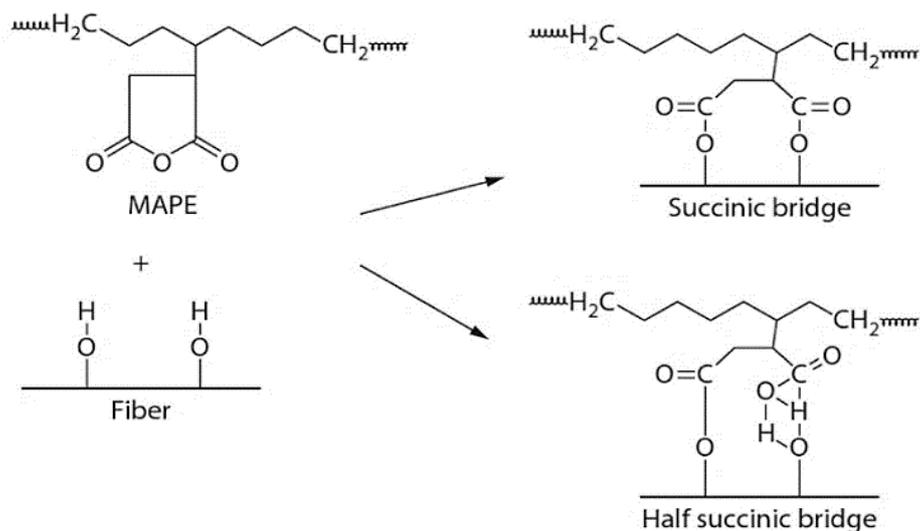


Figure 5: chemical reaction of MAPE and cellulosic fibre [98]

The effects of MAPE on the mechanical properties of jute-reinforce HDPE composites was studied [117]. The results showed, at 30% jute fibre loading, the composite with 1% MAPE exhibit an increase of 47, 26 and 28% in tensile, flexural and impact strength respectively. Moreover, the MAPE treated composites showed an increase in storage modulus and complex viscosity, signifying improved interfacial adhesion. The increase in mechanical properties is mainly due to the formation of an ester linkage between anhydride groups of MAPE and hydroxyl groups of jute fibres. Additionally, the long PE chains of MAPE become compatible with the virgin matrix, lower the surface energies of the fibres and thus, improve the wettability and dispersion within the matrix [118]. In terms of surface properties of MAPP treated fibre, Felix et al. [119] used the dynamic contact angle analysis to measure the surface energy of untreated and MAPP treated cellulose fibres. As expected, the MAPP led to a significantly lower polar part of the free surface energy with 5-8 mJ/m² (compared to untreated cellulose fibres with a value of 42 mJ/m²). This is dependent on the molecular weight of the used MAPP.

Maleated polymers are usually coated on to natural fibres prior to mixing. The acid number, which represents the amount of functionality in a coupling agent, and molecular weight, are two important parameters affecting the coupling effectiveness of MAPP in bio-based polymer composites. Generally, MAPP with a high molecular weight and high acid number effectively improves the mechanical properties of bio-based polymer composites [88].

Grafting MA to PP and PE has proven to be effective to obtain superior mechanical and physical properties OF WPCs. As GELCLAD aims to use biopolymers commercial MA grafted to biopolymers are limited, hence an extra step would be required to produce MA-PLA on a large scale.

4.4. ISOCYANATES

Isocyanates function as useful coupling agents by the formation of covalent bonds between the hydroxyl groups of natural fibres and the isocyanate ($-N=C=O$) functional groups via urethane linkage. The urethane or carbamate linkage between cellulose fibres and isocyanate coupling agents could be formed as illustrated in Fig. 6 [113]. The most common isocyanate coupling agents are also shown in Table 3 [120].

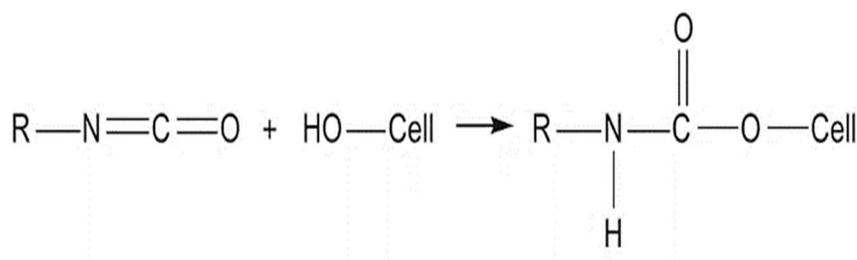
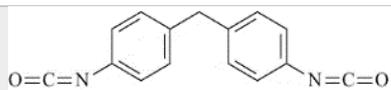
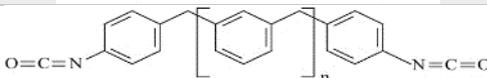
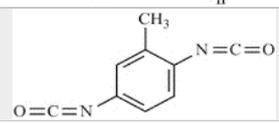


Figure 6: chemical reaction of isocyanate and cellulose [113]

Table 2: isocyanate coupling agents for bio-based polymer composites

Name	Structure
Methylenediphenyl diisocyanate (MDIC)	
Polymethylene polyphenyl isocyanate (PMPPIC)	
Toluene 2,4-diisocyanate (TDIC)	
Hexamethylene diisocyanate (HMDIC)	

Isocyanates are prone to hydrolysis in the existence of moisture. Therefore, blocked isocyanates are used for stopping hydrolysis reaction prior to the reaction with natural fibres hydroxyl groups [121]. For optimum compatibility and dispersibility of the natural fibres in the polymer matrix, different R groups are applied at the other end of isocyanates. Some of the examples include alkyl (e.g. hexamethylene), alkenyl (e.g. 3-isopropenyl- α , α -dimethylbenzyl), aromatics (e.g. toluene and polymethylene polyphenyl), amino acids (e.g. lysine) and plant extracts (e.g. cardanol) [98]. The long and flexible hydrocarbons chains can improve the interfacial bonding between polymer matrix and treated natural fibres via entanglement interlock and van der Waals interactions. Examples are composites of low density polyethylene (LDPE) with a cardanol derivative of toluene diisocyanate (CTDIC) treated sisal fibres, as shown in Fig.7 [122]. Cardanol is the main component of cashew nut shell liquid obtained from the plant *Anacardium occidentale*, which can be found in abundance in tropical sections [120]. The long chain structure of cardanol in CTDIC helps the fibre to have hydrophobic surface, improved compatibility and dispersibility in the polymer matrix.

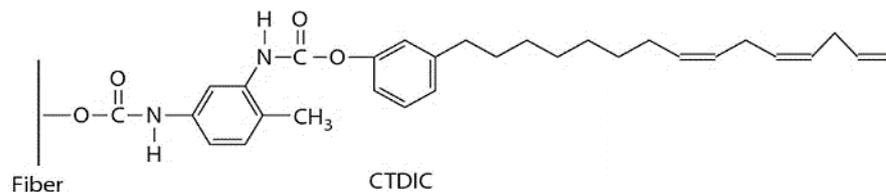


Figure 7: CTDIC-treated sisal fibres

In corn starch-PLA composites, isocyanates groups would react with terminal hydroxyl or carbonyl groups of PLA along with the hydroxyl groups of corn starch to form urethane linkages [123]. The use of isocyanate coupling agents leads to improvements of mechanical properties and reduction of water uptake of composites such as methylenediphenyl diisocyanate (MDIC) treated wheat starch-PLA [123, 124] and MDIC-treated pine fibre-polystyrene [121]. Several conventional isocyanates, such as methylene diisocyanate (MDI), toluene diisocyanate (TDI), 4,4'-methylenedicyclohexyl diisocyanate (hydrogenated MDI), and hexamethylene diisocyanate have been used as a coupling agent [125-127]. However, these isocyanates have found limited use as a biocompatible material because their ultimate hydrolysis products, i.e. their corresponding diamines, such as 4,4'-methylenedianiline and 2,4-diaminotoluene have been found to be a cancer suspect agent or produce hepatitis in man [94].

Isocyanates can provide high durability and superior mechanical and physical properties to the GELCLAD products however several issues rise with Isocyanates especially toxicity and safety concerns.

4.5. TRIAZINE DERIVATIVES

Triazine derivatives such as dichlorotriazines can function as chemical bridges between fibres and polymer matrices. The reactive chlorine atoms on the heterocyclic ring are capable of forming a covalent bond with hydroxyl groups of natural fibres via ether linkage [98], schematically presented in Fig. 8. The reduction of the moisture absorption of cellulose-fibres and their composites, treated with triazine derivatives could be explained by: i) reducing the number of cellulose hydroxyl groups, which are available for moisture gain, ii) reducing the hydrophilicity of the fibre's surface, and iii) limit the swelling of the fibre, by forming a crosslinked network as a result of covalent bonding between matrix and fibre [128, 129].

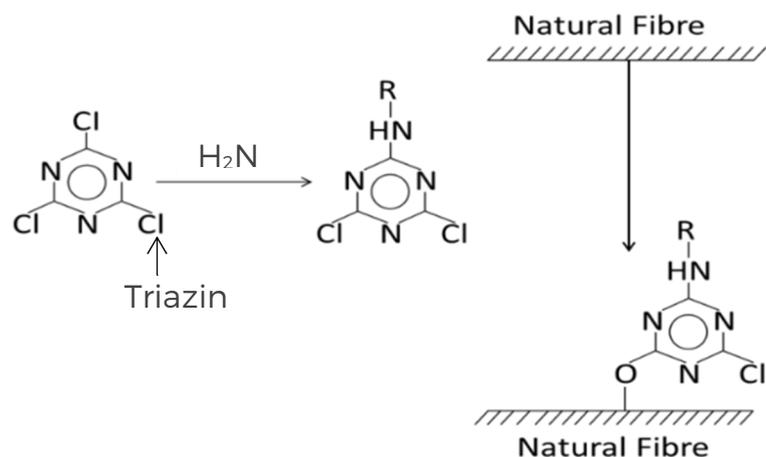


Figure 8: The link between triazine derivatives and cellulose fibre

The highly reactive 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) produced by trimerization of chlorocyanide is manufactured on the scale of several millions tons per year and is among the lowest price reagents [130].

A Triazine derivative was used as a coupling agent for the treatment of cellulose fibres, which subsequently was utilised as reinforcement in polyester resin. This led to improvement in interfacial adhesion and the aging behaviour of the resulting cellulose-polyester composites [131].

A recent US patent [132], which claims a novel triazine derivative with excellent heat resistance and rapid in the cross-linking rate has been published. They claim this could be suitably used as a crosslinking agent. In the invention, it is explained that triazine derivatives and pre-polymer can be obtained by radical-polymerising the monomer with organic peroxide as an initiator.

5

WPC ADDITIVES

Proper additive choices for GELCLAD WPCs are critical to both performance and processing. Different additives can be implemented in the formulation of WPCs to further enhance their physical and mechanical properties. For instance fire retardants, biocides, and nanofillers (ex Nanoclay and metal oxide nanoparticles) [133]. Resistance to fire is crucial for GELCALD especially as their application will be intended for the construction industry where safety requirements are a critical concern.

During a fire wood is extremely vulnerable to burning as a result of the hydrocarbons in the wood that will ignite indirectly during combustion, while the polymer matrix will be begin to degrade with an increase in temperature into various volatile gases that may react with oxygen and further contribute to the combustion behaviour [134]. The most common method to render cellulosic fibres fire retardant is by using P-containing compounds, such as phosphoric acid (PA), tributyl phosphate (TBP), triallyl phosphate (TAP), triallyl phosphoric triamide (TPT), ammonium polyphosphate (APP) , monoammonium phosphate (MAP) and diammonium phosphate (DAP) while the implementation of organomodified nanoclay to design flame retardant polymer nanocomposites has been extensively reviewed [135]. The implementation of APP to produce fiber/PLA composites has shown to significantly improve the flame retardancy and limit oxygen index measurements with minimal influence on the mechanical properties and low loadings [136].

As shown in Fig. 9 for specimens after a limiting oxygen index test, the presence of different intumescent flame retardant additives led to the formation of charred layers. Pure PLA does not form any char and decomposes almost completely [135].



Figure 9: Photographs of PLA specimens after limiting oxygen index tests

The addition of nanoclay into short fiber reinforced PLA bio-composites witnessed higher thermal stability with lower weight loss rate than that of the pure PLA [137], and can have a positive influence mechanical properties, scratch resistance, glass transition temperature and stiffness of the WPCs [134].

The influence of talc (magnesium silicate) on the engineering properties of PHBV-wood composites resulted in an almost 200% improvements to both the Young's and flexural modulus as a consequence of higher compatibility

between PHB and talc than PHB and wood [138]. Similar inorganic filler such calcium carbonate, calcium sulphate, and mica can also enhance properties such as water resistance, creep and stiffness.

Mould, mildew, and stains can have an influence on WPCs properties which has driven manufacturers to consider antifungal biocides that protect either the plastic component and maintain its surface appearance or that preserve the wood component from decay and also reduce moisture absorption. The implantation of coupling agents and compatibilizers into bioWPCS can result in a slower moisture uptake and as well as enhancing the biodegradability rate [139], as a result of stronger interfacial bonds and thus limiting moisture pathways, where an increase in micro cracks can add additional pathways for moisture, enzymatic, and microbial ingress which leads to fiber swelling, increased damage at the fiber-matrix interface, and cracking, further accelerating degradation. A common method to enhance thermoplastic WPCs has been through the addition of anti-microbial agents such as poly-diallyl-dimethyl-ammonium chloride (PolyDADMAC), cetyltrimethylammonium bromide (CTAB), and silver (Ag) which can be easily implemented into BIO-WPCs to enhance the anti-microbial properties and increase their life span [140].

6

BIO-BASED POLYMER COMPOSITES

There is a clear necessity to increase the percentage of bio-based raw materials (i.e. biopolymers/bioplastics and natural fibres) in the formulations of composites with enhanced competitiveness. The increasing number of publications during the recent years including reviews and books [141-146] mirror the growing importance of novel bio-based polymer composites. It is important to note that there are several parameters which must thoroughly be investigated for the understanding of the performance mechanisms of bio-based polymer composites. For instance, fibre/filler volume fraction, orientations, pre-treatments and characteristics of various types of natural fibres, all contribute to the interfacial properties with different thermoset and thermoplastic polymers. Tensile, flexural and impact properties are the most commonly investigated mechanical properties of bio-based composites. Additionally, the long-term performance (creep behaviour), dynamic mechanical behaviour and compressive properties have also been studied for bio-based polymer composites [147]. To further improve the performance, still considerable work has to be carried out, focusing on fibre processing, non-linear behaviour, fibre-polymer matrix adhesion, fibre dispersion, and composite manufacturing with optimised formulations [145]. For instance, for improvement of fibre-polymer matrix adhesion, an additive that is proven to be most effective in reducing creep in PLA and PHA was thiodiphenol, which formed hydrogen bonds at the interface of polymer and fibre, while also tributyl citrate, a plasticiser, led to some, however less obvious, effects [148].

6.1. HIGHLIGHTS OF CRITICAL PROBLEMS WITH BIO-BASED POLYMER COMPOSITES (ECOWPC)

Some of drawbacks with natural fibres and/or fillers, apart from previously emphasised incompatibility with the hydrophobic polymer matrix, are the tendency to form aggregates during processing, and their poor resistance to moisture which is impeding the potential of natural fibres to be used as reinforcement in polymers. The moisture content of the fibres can vary between 5 to 10%. This can lead to dimensional instability in composites and hence deteriorate its mechanical properties. During processing of composites based on thermoplastics, the moisture content can lead to poor processability and porous products [11]. Natural fibres when exposed outdoors could also undergo photochemical degradation caused by ultraviolet light, although resistance to ultraviolet radiation can be enhanced by bonding chemicals to the cell wall or by adding a polymer to the cell matrix [149] (i.e. UV stabilisers).

The UV weathering performance of the different natural fibres and coupling agents in the HDPE based natural fibre composites were investigated [150]. All the weathered samples underwent significant change in the optical

properties, moreover the surface micrographs showed presence of micro voids, cracks and high concentration of exposed natural fibres after 2200 h of UV exposure. The coupling agents had minor influence on the water absorption of weathered composites samples. Flexural stiffness, strength and impact properties of bio-composites weakened after weathering. The coupling agents helped to retain the mechanical properties of bio-based polymer composite after UV exposure [150].

Natural fibres are complex mixtures of organic materials and so, high temperatures would result in variation of physicochemical changes. The production of thermoplastic composites with natural fibres and/or fillers is therefore, limited by the temperatures and processing times that they can be exposed to, before significant degradation. This limits the polymers to lower melt temperature polymers such as polypropylene (i.e. [151-153]), polyethylene (i.e. [154, 155]), polyvinyl chloride (i.e. [156, 157]), PLA (i.e. [158, 159]), and bio-polyesters such as poly(butylene adipate-co-terephthalate) (PBAT) (i.e. [160, 161]), and PHAs (i.e. [162-164]). For improvement of thermal stability, attempts have been made to coat the fibres and/or to graft the fibres with monomers. Grafting is possible as the lignin can react with the monomers. Mohanty et al. [165] have reported that grafting of acrylonitrile on jute improved the thermal stability as evidenced by the increase in the degradation temperature from 170 to 280°C.

A restraint with biopolymers on the other hand, could be the inherent biodegradability. This means it is essential to control the environment in which the polymers are used, in order to prevent the premature degradation. This could be accomplished via control of moisture, nutrients or microorganisms, however in some environments, such as the tropics, this becomes challenging. Additional limitation with some biopolymers is the temperature stability, their application is limited to normal ranges of biological function found in the biosphere [166].

Low strength, high production costs, products quality, and supplier-user relations are some of other general aspects of limitations with bio-based polymer composites. These must be addressed to increase the applications of biodegradable composites [142].

7

CONCLUSIONS AND FUTURE PROSPECTIVE

With the intention of tailoring bio-based polymer composites properties to fit the requirements of ecoWPC frame of GELCLAD, a wide range of potential coupling agents and additives have been reviewed. The identification of suitable coupling agents along with the formulation has major contribution to the success completion of this project.

The development of feasible substitutes to petroleum-based polymeric materials is a compelling new challenge attributable to environmental concerns and the effects of fluctuating oil prices.

Scientific and industrial efforts have been made on a global scale to develop novel technologies to convert these natural resources into new monomers and polymers. Some of these technologies have already generated competitive industrial products with performances comparable to conventional petrochemical polymers.

The emergence of multifunctional bio-based polymer composites (e.g. high modulus, strength, durable, antibacterial and flame retarding characteristics) facilitates their application in new fields, e.g. structural components in construction, automotive, medical and packaging.

A major challenge for biopolymers is the performance gap compared to conventional petroleum-based polymers. As highlighted in this deliverable, considerable research efforts have been made to narrow these performance differences. The scale-up of production of biopolymers, also, is yet to be industrially feasible in some cases such as PHA's.

It is envisaged that the best starting point for a correct approach to the production of bio-based polymer composites is to thoroughly understand the structure, properties, and function of biodegradable polymers, and also how they interact with different natural fibres and coupling agents.

Processing techniques for bio-based polymer composites are well recognised and many of them have been studied. Although, only limited industrial success has been achieved. Challenges still do exist in the emergence of more optimised cost effective manufacturing techniques and material formulations. Addressing these challenges requires interdisciplinary efforts. Additional research for bio-based polymer composites is required to overcome obstacles such as insufficient toughness, moisture absorption, and low durability for outdoor applications. In particular, different weathering conditions, such as temperature, humidity, and UV radiation all affect the service life of these composites.

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