Knowledge Transfer Network

Materials

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TECHNOLOGY OVERVIEW

BIOCOMPOSITES

Knowledge Transfer Networks

Accelerating business innovation:
a Technology Strategy Board programme

FOREWORD

The Technology Strategy Board's Enabling Technologies Strategy 2012-2015[I] includes advanced materials as one of four technologies that "have a key role to play in helping business to develop high-value products and services to meet market needs across all economic sectors, and to generate significant growth in the UK". At the heart of this is a drive to produce advanced materials that are both lightweight and more sustainable whilst maintaining or improving performance for an equivalent cost. In this regard, biocomposites have an integral role to play.

The development and manufacture of advanced materials is also recognised as strategically important to the growth of UK Manufacturing in the Technology Strategy Board's High Value Manufacturing Strategy[II], and composite materials are included within this.

Advanced biocomposite materials will enable solutions for a growing market and will help companies meet societal challenges. Exploitation of these materials, with improved properties, will open up new market opportunities, particularly in applications where lightweighting and environmental performance are key considerations.

This joint report, commissioned by the Materials KTN and authored by NetComposites, describes current and emerging biocomposites and demonstrates that these materials are now starting to find applications across a wide range of industry sectors.

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[I] Enabling Technologies Strategy 2012-2015, Technology Strategy Board, November 2012, www.innovateuk.org

[II] High Value Manufacturing Strategy 2012-2015, Technology Strategy Board, May 2012, www.innovateuk.org

Biocomposites: Technology Overview is a major revision of Best Practice Guide, Natural Fibre Composites, by Brendon Weager, NetComposites, commissioned by Materials KTN, issued March 2010.

This revision has been jointly undertaken by Materials KTN and NetComposites Ltd.

EXECUTIVE SUMMARY

Composite materials derived from natural, renewable sources have received significant interest in recent years, in particular due to the increased awareness of and drive towards more environmentally sustainable technologies. In many cases bio-based materials offer weight reduction, added functionality (e.g. damping / impact absorption) and occupational health benefits. A significant market driver for high volume applications is the potential to disassociate material costs from the fluctuating price of oil and energy.

This guide provides an overview of biocomposites, and the natural fibres, bio-based polymers and bio-based core materials used to produce them, and presents the current best practice in materials, processes and applications. Sources of information include technical papers, articles, online information and discussions with experts. The term "biocomposite" is used here to denote fibre-reinforced polymer composite materials where the fibres and/or matrix are bio-based.

Hemp, jute and flax are common natural fibre reinforcements in biocomposites and have good mechanical properties. Fibre quality is influenced significantly by the harvesting and processing steps and there is a move to reduce the on-field processing to improve consistency and reduce costs. Loose fibre, non-woven mats, aligned yarns and woven fabrics are possible forms of natural fibre for composites, with aligned variants offering the best mechanical properties. Fibre treatments such as acetylation can be used to reduce moisture uptake and improve compatibility with polymers. Synthetic bio-based fibre reinforcements, such as regenerated cellulose, are also available and offer higher consistency.

A number of bio-based polymers are commercially available including thermoplastics such as starch, PLA and PHB, which are used in packaging, and thermosets from plant oils and sugars. In the short term, blended resins containing both bio and synthetic constituents offer a good compromise of performance and environmental impact.

In most cases, natural fibres have lower environmental impact than glass fibres due to reduced CO_2 emissions and energy consumption during production. During the use phase, natural fibres can have a positive environmental impact due to their low weight. At the end of life, natural fibre composites can be recycled, biodegraded (when used with biodegradable polymers), or can be incinerated for energy recovery.

A wide range of applications exist for natural composites, most notably in the automotive, construction, consumer and leisure markets. Commercial applications of natural fibre-synthetic polymer composites include WPC decking and outdoor furniture and automotive parts such as door liners and trim panels. The demand from designers, manufacturers and consumers for environmentally friendly products will inevitably drive the rapid development of other biocomposite materials and products.

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1 INTRODUCTION

Composite materials derived from natural, renewable sources have received significant interest in recent years, in particular due to the increased awareness of and drive towards more environmentally sustainable technologies. In many cases bio-based materials offer weight reduction, added functionality (e.g. damping / impact absorption) and occupational health benefits. A significant market driver for high volume applications is the potential to disassociate material costs from the fluctuating price of oil and energy.

The environmental benefits of bio-based material sources include low embodied energy, CO_2 sequestration, reduced depletion of fossil-based resources and a positive impact on agriculture.

Natural fibres, such as hemp, flax, jute and kenaf, have good strength and stiffness, whilst being significantly lighter than conventional reinforcements such as glass fibres, and they are relatively low cost and biodegradable. Natural fibres are currently used in significant quantities, in particular in automotive interior components, to reinforce synthetic polymers such as polypropylene (PP).

A number of naturally-derived polymers and resins have been launched commercially, the most notable being polylactic acid (PLA) from corn starch and polyfurfuryl alcohol resins from waste sugarcane biomass. However, many more types are currently under development, from sources including starches and crop oils.

More recently, combinations of these natural fibres and bio-based polymers have been shown to have appealing composite properties, offering the enticing prospect that fully bio-based composites are an increasing commercial reality.

This guide provides an overview of natural fibres, bio-based polymers and biocomposites, including their properties, processing and applications, and aims to give a guide to the current best practice in this emerging area of sustainable composite materials technology. Although many types of natural fibres are available, this guide focuses on bast fibres as these are most suitable for composites. The information has been gathered from sources including technical papers, articles, online information and discussion with experts from industry and academia.

Standards, claims and regulation are important in bringing bio-based products to market, but are not addressed in this Technology Overview as they are covered in the recently published *PAS 600:2013 Bio-based products – Guide to standards and claims* [1].

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2. NATURAL FIBRES

2.1 TYPES OF NATURAL FIBRES

A wide range of natural fibres exist and they can be classified into three main groups – plant, animal and mineral (Figure 1). The most interesting fibres for composite reinforcements are from plants, in particular bast, leaf and wood fibres. Bast fibres, such as flax, hemp, jute and kenaf, are taken from the stem of the plant and are most commonly used as reinforcements because they have the longest length and highest strength and stiffness. Flax and hemp are of particular interest in the UK and Europe because they are native to the region.

These types of plant fibres are composed principally of a combination of cellulose, hemicellulose and lignin. From an environmental perspective, these fibres are biodegradable, recyclable and are 'carbon positive' since they absorb more carbon dioxide than they release [2].

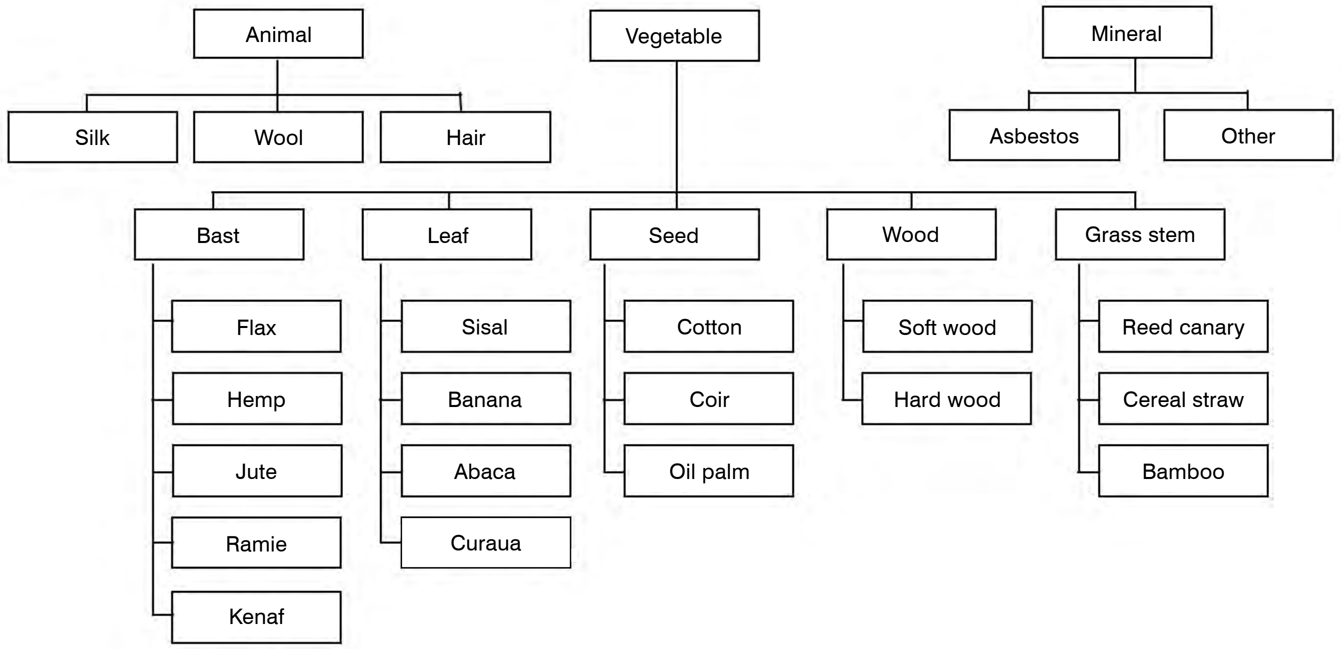

Figure 1: Types of natural fibre, from [3].

2.2
GROWING AND HARVESTING

The growing stage is an important stage in natural fibre production because it has a great influence on the quality and consistency of the fibre. In particular, the weather conditions can significantly affect the quality of the crop and the consistency between different locations and from year to year. It is good practice for growers to retain significant quantities of fibre in buffer storage in case of a poor harvest.

Flax and hemp can be successfully grown in the UK and Europe due to the temperate climate, although hemp is considered to be easier to cultivate because yields are higher per hectare and it has greater resistance to drought [4]. Hemp and flax plants can yield both fibres from the stem and oil from the seed (e.g. linseed) but a range of crop species exist for different end uses and the best fibres will be obtained from those species which have been selected and bred specifically for that purpose. For example, in a study of 92 flax varieties, the Regenboog type was found to be favourable for producing high quality flax fibre on cotton spinning systems [5].

At optimum maturity the crop is cut or 'pulled' and spread out on the field to dry (Figure 2). A UK-based study found that the optimum harvesting method for flax was desiccation at the mid-point of flowering ± 3 days (early to mid-June depending on variety) and application of 4 litres/hectare of a glyphosate-based herbicide, followed by harvesting approximately 8 weeks after desiccation [6].

Other non-European crops include jute, sisal, kenaf, ramie and curauá. Of these, jute is the most commonly used natural fibre in biocomposites and is predominantly grown in Bangladesh, India and China. Sisal is native to the Yucatan but Brazil is now the main producer and curauá is grown in the Amazon region but can also be found in other areas where the rainfall exceeds 2,000 mm p.a. [7].

Figure 2: Pulling of flax crop (photo used with kind permission of Mr Marian Planik, WFB Baird Poland Sp. z o.o.).

2.3
PROCESSING OF BAST FIBRES

Figure 3 shows a cross-section of a typical bast stem and illustrates that the useful fibres are present as bundles towards the outer of the stem. For composite reinforcement, the aim is usually to obtain 'technical fibres', which are 50-100 μm in diameter and can be 100-300 mm long. These technical fibres are actually themselves bundles of approximately 40 elementary fibres (cells) which may be 10-20 μm and 20-50 mm long.

The most important consideration in processing natural fibres is to obtain the desired level of refinement without causing excessive damage. Mechanical processing tends to be aggressive which can induce kink bands in the fibres, thereby creating weak points, and can break the fibres into short lengths, thus reducing their reinforcing potential.

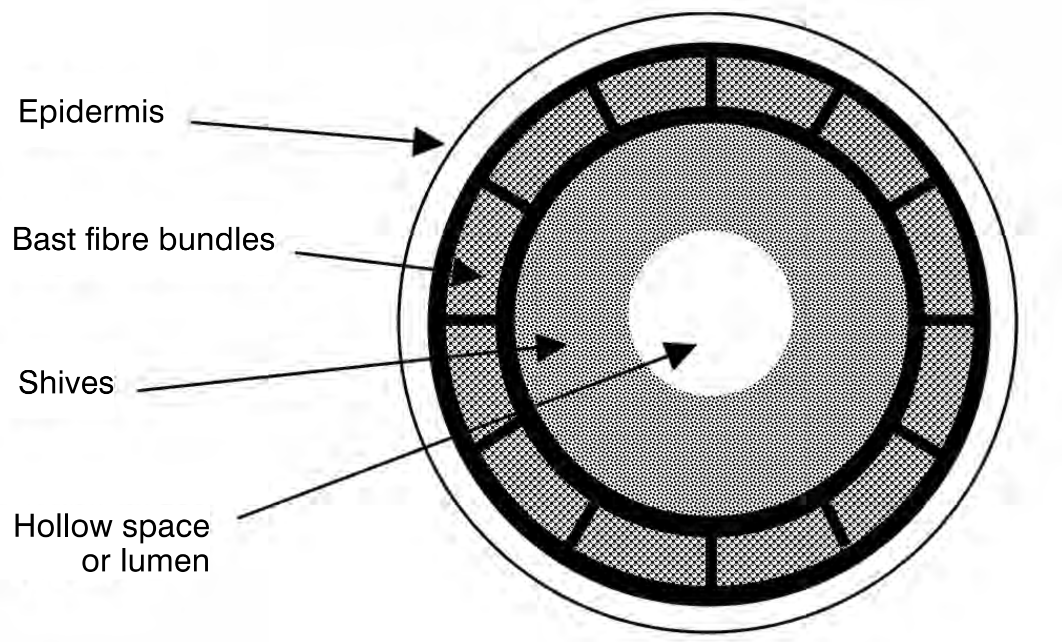

Figure 3: Cross-section of a bast stem [8].

2.3.1 FLAX PROCESSING

The extraction of fibres from the flax plant usually follows these steps:

RETTING

Retting is a biological process during which the pectinous matter in the woody stem is broken down by enzymes and bacteria, allowing the fibres to be removed more easily and improving the fibre fineness. Correct retting is of great importance; under-retting means that the fibre bundles cannot be separated from the wood easily and over-retting results in a weakened fibre.

The most common retting process is called dew retting, whereby the cut stems are simply left on the field and the action of dew, sun and fungi causes the desired biological process. This process can take 3-6 weeks, depending on the weather conditions, and action may not be uniform so the straw is often turned 2-3 times during the period. The main drawback of dew retting is that the fibre quality can be inconsistent depending on the weather conditions and also the process is not feasible in drier climates, for example in Southern Europe [9]. An alternative process is water retting, where the stems are immersed in ponds or rivers. This technique is employed in China, India and some parts of Eastern Europe [10].

In recent times, significant efforts have been made to develop chemical or enzymatic retting processes which are fast, controllable and environmentally sound [11-12]. These processes typically involve placing the harvested straw in temperature controlled tanks and treating them with chemicals, such as sodium hydroxide or sulphuric acid, or enzymes which break down the pectins very quickly (as little as 1-2 hours) but careful control is required to prevent deterioration. For example, a UK-based study of 8 commercial enzyme products found that Bioprep L, an alkaline pectinase supplied by Novo Nordisk A/S, Denmark, produced very good results overall, whilst some led to a significant reduction in fibre strength [6]. The cost of enzymes at approximately £1/kg was a concern. A study in Poland also found Bioprep L to be suitable, whilst cellulolytic agents were found to roughen the fibre surface [13], which may promote improved fibre-matrix adhesion. Other flax fibre separation techniques under investigation include ultrasound and steam explosion [14].

BREAKING AND SCUTCHING

Once retted, the straw is dried, baled and collected from the field. Then, inside the fibre processing facility, the bales are opened and the straw is passed through fluted rolls to break up the woody material into small pieces (Figure 4). The broken pieces of shive are then removed in a scutching mill, where flat steel blades beat or scrape off the shive. Although of less interest for fibre-reinforced composites, the shive can be used with lime cement to make bricks or can be used as animal bedding. During this stage, the seeds can also be collected and are most commonly used for animal feed.

Figure 4: Bale opening at the start of a flax processing line (photo used with kind permission of Mr Marian Planik, WFB Baird Poland Sp. z o.o.).

HACKLING

Hackling involves mechanically combing or carding the fibre bundles to separate out the short and long fibres, whilst aligning them and removing further debris. The fibres can be used in their loose form or can be spun into yarns and woven into textiles. The long fibres tend to be used for higher quality applications (e.g. linen cloth for apparel and furnishings) and therefore command high prices (e.g. £4/kg), whilst the short fibres are less valuable (50p-£1/kg) and are used in ropes, carpets, insulation and paper. Both types can be used for composite reinforcements, although it is usually only economically viable to use the cheaper short fibres. Figure 5 illustrates a typical process route for flax and the products obtained at each step.

Figure 5: Production of bio-based materials and products from flax plant. © British Standards Institution (BSI – www.bsigroup.com). Extract reproduced with permission. From [1].

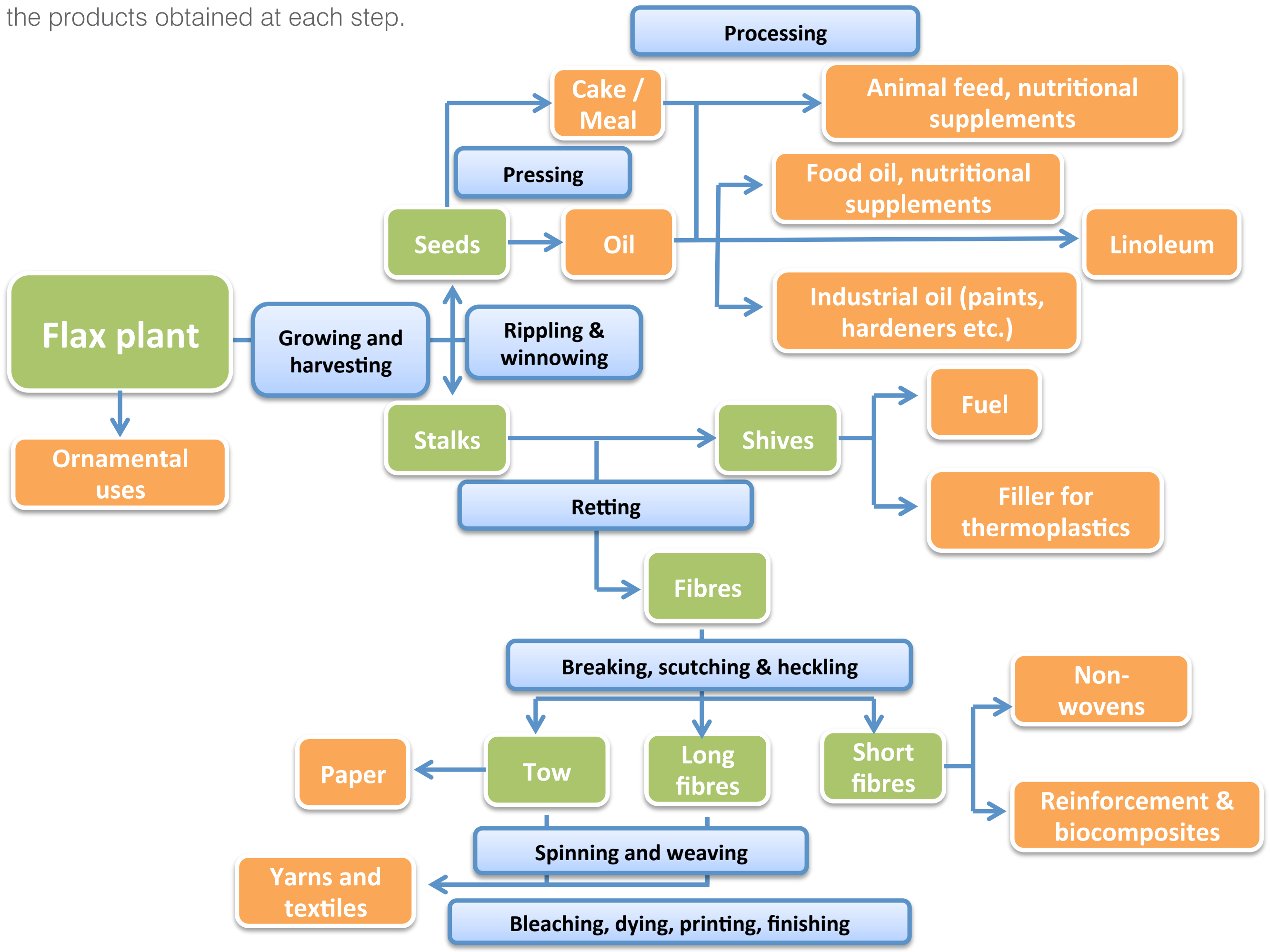

Figure 6 shows the typical proportions of different products obtained from processing flax. It can be seen that fibre products account for approximately 36% of the total crop yield of 5,600 kg/hectare, with the rest being shive and grain.

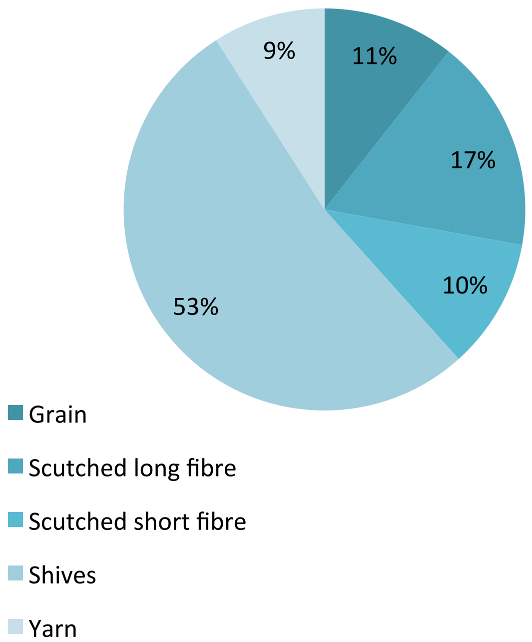

Figure 6: Proportions of different products obtained from processing flax (total 5,600 kg/hectare), data from [15].

2.3.2 HEMP PROCESSING

Whilst it is possible to process hemp in a similar way to flax as described above, the machinery for hemp tends to be more heavy duty due to the stem being thicker [16]. The (dew) retting process also takes longer, typically delaying collection until October when the wetter weather makes drying and collection difficult. Therefore, it is becoming more common to miss out the retting stage and process hemp in its 'green' state [17], sometimes with enzymatic treatment but more often without. This significantly reduces cost and lead time, whilst avoiding the climatic uncertainty associated with retting. In a study comparing the processing of retted and unretted hemp, it was found that the yield, length distribution and strength of fibre were the same from both types but unretted fibre was coarser and contained almost 4% impurities, compared with 2% for retted fibre [18]. The light colour of unretted fibre and low amount of fungal material were considered a marketing advantage.

Typical modern hemp processing facilities, such as those supplied by Van Dommele Engineering/Robert S Maynard Ltd [19], include the following:

- Opening – pre-opening of the straw bales.
- Decorticating – hammer mills break up the straw and separate the fibres and shive.
- Fibre refining – cleaning of the technical fibres, often several separate steps in series.
- Duvex – cylindrical rotating drum/sieve which removes the very short fibres.
- Dust removal – extraction of dust.

Whilst for composite reinforcement it may be preferable for the natural fibres to have very low impurity (shive) content, the additional processing cost required to remove all impurities can be prohibitive.

2.3.3 JUTE PROCESSING

Jute is the second most important natural fibre after cotton [20]. The way in which the fibres are extracted from the plant follows the same route as that used for flax fibres.

Bangladesh, India and China are the main producers of jute fibre. The plant is rain fed so yield can be affected by the timing of the monsoon. The plant grows to about 3.0-3.6 m high in 100-120 days. Two main varieties are used: Corchorus Capsularis and C. Olitorius. Both varieties have a tendency to branch but the best fibres are obtained from unbranched stems. The plants are harvested once the fruits have set.

Jute fibres contain 10-13% lignin and this delays the action of microbes in the retting process. The stems are cut and the leaves removed (often by hand) before retting in ponds or canals – a slow flow of water is preferable to using stagnant water. The bundles of fibre are held fully immersed e.g. by a bamboo scaffold. Retting typically takes 10 days but it is down to the skill of the operator to decide when the process has proceeded far enough. The fibres are then extracted by hand from the retted stems. Once extracted the fibres are washed and left to dry in the sun [20].

2.3.4 FURTHER PROCESSING TO OPTIMISE PROPERTIES

Following processing, flax, hemp and jute fibres are discontinuous (typically 1 – 100 mm long), randomly oriented and may contain a small amount of impurities (e.g. shive). For some processes and applications, this short, loose fibre form is appropriate. For injection moulding it is sometimes necessary to chop the fibres into a prescribed length, e.g. 2, 4, 10 or 25 mm [21-22]. For press moulding, the natural fibres are carded and needle-punched to produce non-woven mats or fleeces, with typical areal weights of 200-1000 g/m2.

It is well known that to achieve optimum mechanical strength and stiffness in a composite, the reinforcement fibres should be continuous and aligned in the direction of the applied load. The same is true for natural fibres.

The carding and cross-lapping process involved in manufacturing needle-punched fabrics introduces a limited amount of fibre alignment. However, in order to obtain continuous, aligned natural fibre reinforcements, the fibres must be carded and drawn into a sliver (a loose, aligned tow), then either a) spun into a continuous yarn, followed by weaving (or similar), or b) formed into unidirectional tapes or aligned multi-axial fabrics.

Whilst many natural fibre yarns and textiles are commercially available, in particular for carpet backing, bags, upholstery, clothing etc., these are generally unsuitable for composite reinforcement. The yarns typically have a high level of twist in order to impart good tenacity (strength) but this causes the fibres to be off-axis by the angle of twist (which can be up to 30^{o} or more) and the fibres are held tightly together making resin impregnation and wet-out difficult. Several studies [e.g. 23] have investigated the effect of twist in flax yarns and shown that as twist increases the dry yarn strength increases but the composite strength reduces (Figure 7). The optimum yarn twist was approximately 90 turns/m.

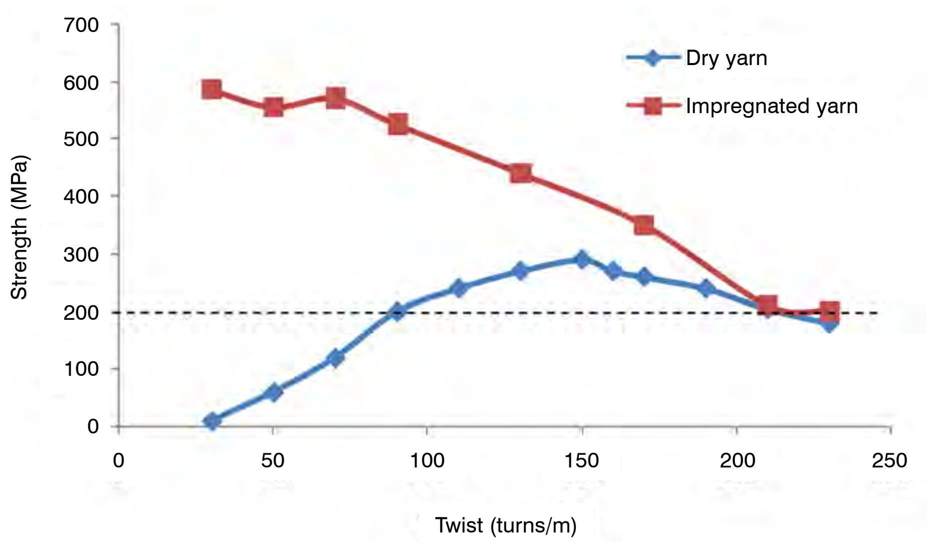

Figure 7: Effect of yarn twist on dry yarn strength and impregnated yarn (composite) strength. Minimum yarn strength is 200 MPa. Data from [23].

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Figure 8: A selection of flax reinforcement fabrics (courtesy of Composite Evolution Ltd).

The UK based COMBINE project [24] and the European NATEX [25] project both worked on the development of natural fibres textiles for composite reinforcement. NATEX examined enzymatic and chemical methods of fibre separation but the methods investigated either resulted in a loss of fibre strength or were too expensive to be used commercially.

Furthermore, a number of projects are also using natural reinforcements to develop biocomposites, which include the UK funded UK-BIOCOMP [26] and FRBioComp [27] projects and European Commission funded projects Bugworkers [28] and BioBuild [29].

An alternative to woven or stitched fabrics is to use the natural fibres in their aligned roving state, for example to produce laid flat ribbons, spread tow fabrics or loosely stitched aligned mats. These materials tend to be lower cost and produce better fibre volume content, which, along with the reduced twist, results in improved mechanical properties. However they are more difficult to handle in composite processes.

A number of woven and unidirectional / biaxial flax and jute fabrics, tapes and braids made with 'twistless' yarns are now commercially available, such as those supplied by Composites Evolution under the name Biotex® (UK), the Bcomp ampliTex® range (Switzerland) and Lineo's FlaxTape (France). Groupe Dehondt produce a flax roving which is not twisted under the tradename NATTEX ® [30] and other fabrics in their FLAX TECHNIC range. Tilsatec (UK) is also working on wider unidirectional tapes.

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2.4
FIBRE PROPERTIES

Table 1 compares typical properties of various natural fibres and glass fibres. Natural fibres have approximately half the density of glass fibres and have similar tensile modulus, but they have lower tensile strength and significantly higher moisture absorption. When taking density into account, the specific modulus (modulus divided by density) of flax and hemp fibres exceeds that of glass fibre, making them particularly interesting for engineering composite materials. It has been estimated that substituting glass fibres with natural fibres can reduce the weight of a composite by up to 40% which, in the automotive sector, can lead to substantial benefits in fuel efficiency [22-32].

In addition to their appealing mechanical properties, natural fibres are non-irritating making them safer and easier to handle, and tend to be non-abrasive resulting in reduced wear on tooling and manufacturing equipment. Natural fibres are also biodegradable and/or recyclable, depending on the desired end-of-life process route.

The main shortcomings associated with natural fibres as composite reinforcements are the relatively high moisture uptake, which can lead to swelling, rotting and reduced mechanical properties, the low impact resistance, the relatively low temperature capability (decomposition usually occurs at approximately 200 ^{o}C) and the maintenance of acceptable levels of quality control. Natural fibres are hydrophilic ('water loving') in nature which can lead to compatibility issues when combining with hydrophobic ('water hating') polymer matrix materials. Waxy compounds can also be present on the surface of the fibres, making it difficult to achieve strong fibre-matrix bonding. However, work is underway to address such issues, including the use of fibre treatments.

FIBRE	DENSITY (g/cm^3)	TENSILE MODULUS (GPa)	SPECIFIC MODULUS, (GPa/g/cm^3)	TENSILE STRENGTH (MPa)	ELONGATION TO FAILURE (%)	MOISTURE ABSORPTION (%)
Flax	1.4	60-80	43-57	500-900	1.2-1.6	7
Hemp	1.48	30-70	20-47	300-800	1.6	8
Jute	1.46	20-55	14-38	200-800	1.8	12
Ramie	1.5	44	29	500	2	12-17
Coir	1.25	6	5	220	15-25	10
Sisal	1.33	9-38	7-29	100-800	2-3	11
Cotton	1.51	6-12	4-8	300-600	3-10	8-25
Glass	2.55	73	29	2400	3	-

Table 1: Typical properties of natural fibres and glass fibres, from [4-33].

2.5
FIBRE TREATMENTS

In order to overcome some of the disadvantages of natural fibres, in particular the poor bonding to polymers, the high moisture uptake and the limited thermal stability, a wide range of physical, chemical and additive treatments which modify the fibre characteristics have been investigated.

Of the treatments described below, acetylation is generally considered to have the most potential for natural fibres because it significantly improves the moisture resistance, continuous processing is possible and the fibre strength and stiffness are not reduced. The Duralin® process is also successful for flax fibres in particular.

2.5.1 PHYSICAL TREATMENTS

Physical treatments such as plasma and corona discharge can improve the functional properties of natural fibres. Plasma treatment in oxygen can roughen the surface. Low-temperature plasma treatments improve the surface of natural fibres by causing chemical implantation, etching, polymerisation, free radical formation and crystallisation [34]. For example, the wettability of wood fibres has been found to improve significantly with increased level of corona treatment [35]. Plasma treatment is regarded as being an environmentally friendly and cost effective technique, although some of the gases employed can be harmful to the environment. There are problems with scaling-up plasma treatments for industrial use. Atmospheric pressure plasma processes offer the prospect of being a continuous operation but are currently limited in availability and scope.

Hydrothermal treatments can be used to reduce moisture uptake and improve thermal resistance. For example, the Duralin® process, developed specifically for flax, involves heating 'green' flax straw in a pressure vessel for 15 minutes at 160-180^{o}C, drying and then heating in air for 30 minutes at 180^{o}C to 'cure' [7,39]. Moisture uptake is significantly reduced by mechanisms including extraction of hemicellulose during hydrothermolysis, cross-linking of reaction products and increased cellulose crystallinity. In addition, the thermal degradation of Duralin® flax during composite processing is significantly lower than untreated fibres. This process also eliminates the need for dew retting, discussed previously.

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2.5.2 CHEMICAL TREATMENTS

Alkali treatment is a common method to clean and modify the surface of natural fibres to promote enhanced fibre-polymer adhesion. Mercerization is a traditional alkali treatment based on sodium hydroxide (NaOH, caustic soda), which improves the take up of dye in textile processing. A number of studies have found that alkali treatments can improve the properties of natural fibres and the interfacial adhesion to polymers [36, 37].

Acetylation is a treatment of particular interest for natural fibres. In this treatment, acetic anhydrides substitute the cell wall hydroxyl groups of a natural fibre with acetyl groups, rendering the surface more hydrophobic and thus less susceptible to moisture uptake and biological attack and more compatible with polymer matrices [38]. Acetylation is commonly applied to wood to improve dimensional stability and environmental resistance. A typical process involves soaking the fibres in acetic acid, then treating them with acetic anhydride and then a final washing stage [7]. If done properly, fibre properties such as strength and modulus are not reduced.

Isocyanates can be used as coupling agents to improve the bonding of natural fibres to polymers. For example, the strength and stiffness of wood-polypropylene (PP) composites can be increased by treating the fibres with polymethylene-polyphenyl-isocyanate [35]. Bio-based isocyanates such as lysine diisocyanate also make effective coupling agents and are of particular interest, due to health concerns over synthetic isocyanates. For example, lysine diisocyanate has been successfully used to improve the mechanical properties and water resistance of bamboo fibre-polylactide composites through enhanced fibre-matrix interfacial adhesion [40].

Organo-silane coupling agents are commonly used in conventional composite materials and they can also improve interfacial adhesion in natural fibre composites. They work by acting as a chemical bonding link between the cellulose and the polymer, providing molecular continuity across the interface. For example, chemical modification of henequen fibres with an alkali treatment followed by immersing in a 0.033 weight% aqueous silane solution has been found to result in much stronger fibre-matrix interaction [41].

2.5.3 ADDITIVE TREATMENTS

Improved natural fibre-polymer matrix interaction can be achieved by impregnating the natural fibres with compatible polymers. This can be achieved using a solvent exchange technique or by infusing monomers into the fibres and polymerising them in-situ using a catalyst, heat or radiation [34]. For example, improved interfacial properties of high density polyethylene (HDPE)-henequen (a close relative of sisal) composites have been reported by impregnating the fibres with HDPE dissolved in xylene.

2.6
OTHER NATURAL FIBRES

Regenerated cellulosic fibres such as viscose and rayon are bio-based, although it is arguable as to whether they should be considered to be natural. These are made by dissolving cellulose, for example from wood fibre pulp, in a solvent and then spinning yarns from the solution [42]. Regenerated cellulosic fibres can provide higher impact strength and a much more consistent fibre / fabric than bast fibres in biocomposites. They are being marketed for composites by several companies including Porcher Greenlite and BioMid.

There is significant interest in naturally sourced nanofibres, or nanocellulose, as reinforcing fillers. However this is outside the scope of this report.

Other vegetable fibres which are of industrial interest are ramie, sisal, kenaf, coir (from coconut husks) and banana leaf fibre. There is also work directed at using animal fibres, such as wool and chicken feathers [45]; and there are attempts to produce spider silk in-vitro since it has excellent mechanical properties [46].

Figure 9: BioMid reinforcement yarn and fabric. A 'second generation' bio-based fiber made from by-products of the lumber industry. Photo by Linda Taylor.

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3 BIO-BASED POLYMERS AND RESINS

The development of polymers from renewable resources has received considerable attention in recent years, in particular due to volatility of crude oil prices and the desire to avoid landfill disposal. It is possible to synthesise both thermoplastic and thermosetting polymers from bio-based chemicals. Typical sources are plant oils and starches. The market demand for natural polymers is strong and a number of bio-based polymers are now available in large quantities and are finding commercial applications. European Bioplastics have predicted that the market will grow from 1.4 million tonnes in 2012 to approximately 6.2 million tonnes in 2017 [47]. A Market Study by Nova Institute [48] suggests that much of this development is expected to be in drop-in biopolymers (chemically identical to their petrochemical counterparts but at least partially derived from biomass) such as bio-based PET, polyethylene and polypropylene derived from bio-ethanol from sugarcane.

Industrial biotechnology (IB) is playing an increasingly important role in global markets, where bio-based systems and processes are rapidly gaining strength and scale. This will bring economies of scale for bio-based chemical feedstocks for the resin formulators. The IB market is projected to grow up to £360bn globally by 2025 with up to a £12bn share in the UK [49].

It is important to note the distinction between bio-based and biodegradable polymers because not all bio-based polymers are biodegradable and vice versa. Bio-based polymers are polymeric materials which are made from natural, renewable raw materials, whereas biodegradable polymers are those which can be broken down by microorganisms at end of life. There are also significant differences between degradable, bio-degradable and compostable polymers. Degradable polymers break down into smaller molecules or fragments through chemical reactions initiated by, for example, heat or UV light. The process is enhanced by mechanical stress. Biodegradable polymers can be converted by naturally occurring microorganisms (microbes such as bacteria, fungi or algae) into biomass, carbon dioxide and water and, therefore, are considered to be more environmentally friendly than degradable polymers. However, the biodegradation process can produce methane and the waste can contain toxins. For a polymer to be considered compostable, it should break down at the same rate as other compostable materials such as for example paper and should result in a compost-like material which supports plant life and does not contain toxins. In some cases biodegradation or composting require special environmental conditions, such as a particular type of bacteria, temperature and/or humidity, which can only be achieved in industrial facilities.

3.1 THERMOPLASTIC BIO-BASED POLYMERS

3.1.1 STARCH

Starch from corn, rice, wheat or potatoes can be used to produce polymers and is an inexpensive and abundant base material [34]. The preferred grades of starch for polymer production are high in amylose content, produced through selective breeding. Starch-based polymers tend to be sensitive to water, highly brittle and have low heat stability but these issues can be overcome by hydrophobic modification (e.g. acetylation) and using plasticisers. Acetylation of starch, to produce starch acetate, reduces brittleness by reducing the modulus and increasing strength and elongation. Plasticising with polyalcohols such as hydroxypropyl to form long alkyl chains (internal plasticising) or triacetine (TriAc) and triethyl citrate (TEC) (external plasticising) improve the water sensitivity, reduce the glass transition temperature (Tg) and make the starch more processable [50]. Starch can also be plasticised with water, sorbitol, glycerol and urea but the sensitivity to water is not improved. Typical applications of starch polymers include packaging materials such as compostable foams, trays and films. Starch-based polymers are compostable.

3.1.2 CELLULOSE

Plant cellulose can be used to make cellulosic plastics by using the acetylation process. Examples include cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) [34]. Cellulose diacetate became a major thermoplastic moulding material in the early 20th century and is still used to make some plastic combs and toothbrushes. Cellulose is inherently biodegradable, environmentally friendly and continuously renewable.

3.1.3 POLYESTERS

Biodegradable thermoplastic polyesters can be derived from fossil fuel and renewable sources. For example, polycaprolactone (PCL) is a polyester which is biodegradable but derived from fossil oil, whereas polylactic acid (PLA) and polyhydroxyalkanoates (PHA) are biodegradable polyesters which are made from bio-based sources.

PLA is a versatile bio-based polymer produced through the fermentation of sugars or the conversion of starch, for example from corn. It has been used for many years in the biomedical sector for drug encapsulation and medical devices but has only recently become economically feasible for wider engineering use [34]. PLAs are available commercially from a number of suppliers, although the most well-known is Natureworks® in the USA. PLA is used principally in food packaging such as trays, films, cups and bottles, but other applications include textiles and fibre filling for cushions. Different types are available for different processes or applications, for example injection moulding grades, film grades, fibre grades, etc. PLA is compostable in industrial composting facilities.

PHAs are produced through fermentation by micro-organisms fed on simple sugars. Yield is improved by depleting the nitrogen content of the broth so the micro-organisms cannot synthesise proteins. The polymer has to be extracted by solvent. It is suitable for films, bottles and containers. The most common examples of PHAs are polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV) and the copolymer polyhydroxybutyrate-co-hydroxyvalerate (PHBV). PHBV in particular is highly crystalline and has similar melting temperature (Tm) and glass transition temperature (Tg) to PP [34], although it is stiffer and shows a lower elongation to break. The principal commercial source of PHA is TianAn Biologic Materials in China. In the USA Metabolix are producing PHA under the tradename Mirel. Typical applications are packaging, agriculture/horticulture and marine/aquatic applications and different grades are available for film (blown and cast), injection moulding and sheet extrusion/thermoforming. PHAs are biodegradable and compostable. The FP7 funded project Bugworkers has developed a process for producing PHAs using non-food grade sugars from the hydrolysis of wheat straw [51]. This project has also used a novel solvent extraction method for PHB which does not require halogenated solvents.

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3.1.4 LIGNIN

Lignin is a natural matrix material which binds the strong and stiff cellulose units together in, for example, natural wood. Once separated, it can be chemically modified or blended to produce a thermoplastic-type polymer which can be heated and processed like synthetic thermoplastics [52]. Lignin can be in the form of a brown powder, but more often it is a gummy mixture with a wide range of molecular weights. It is a by-product of the pulp industry and the volume arising worldwide is about 50 million tonnes per year. An example of the use of lignin as a bio-based polymer is TECNARO (Germany) who supply lignin-natural fibre compounds for injection moulding and extrusion. Lignin is biodegradable.

With the decline of the paper industry, paper mills and woodland owners are looking at developing and commercialising other products and technologies utilising wood, and lignin could become an important feedstock for production of many chemicals. Innovation Norway and the Technology Strategy Board signed a Memorandum of Understanding in February 2011 to work more closely in the areas of industrial biotechnology and biorefining [53]. A significant area that is being developed is uses for lignin and woody biomass generally in biorefining.

Bio-based polymers tend to cost more than synthetic polymers (Figure 9) but the prices of bio-based polymers are expected to reduce as production increases and the prices of synthetic polymers are expected to increase as crude oil reserves diminish.

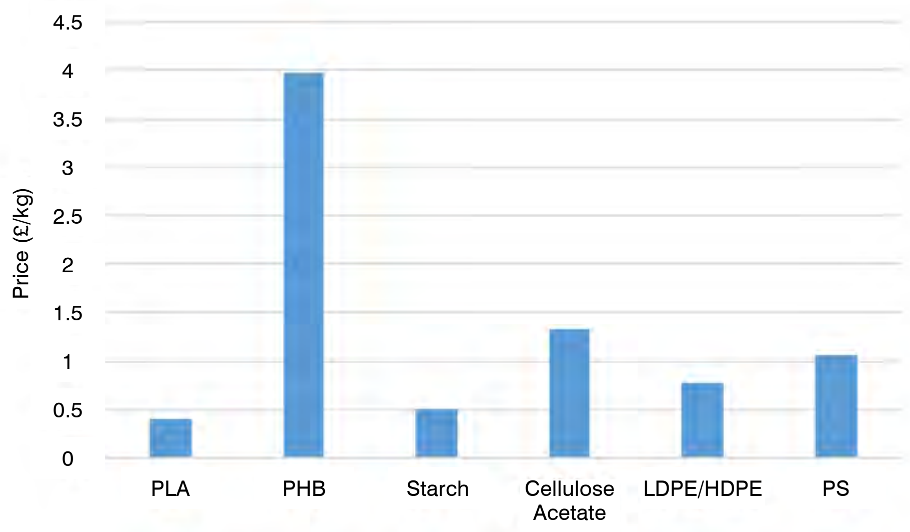

Figure 10: Indicative prices of bio-based polymers compared to synthetic polymers, data from [54-57].

3.2 THERMOSETTING BIORESINS

3.2.1 PLANT OILS

A wide range of plant and vegetable oils can be converted into thermosetting bioresins. Vegetable oils are triglycerides (esters of different fatty acids) which can be functionalised with reactive groups such as hydroxyl, carboxyl, amine and epoxy and, hence, can be cross-linked to form rigid polymers [7]. Synthetic chemical cross-linkers are still needed, with various isocyanates, amines, polyoles and polycarboxylic acids being used. Current research is concentrating on finding isocyanates from a biological source [0]. The selection of feedstock tends to be geographically dependent, with US developments tending to focus on US native crop oils such as soybean, while linseed, rapeseed and sunflower receive more interest in Europe.

Researchers at the University of Delaware (US) have undertaken a considerable amount of development work in soybean oil-based resins, in particular through the Affordable Composites from Renewable Sources (ACRES) programme [58]. For example, polymers based on acrylated epoxidised soybean oil and maleinized hydroxylated soybean oil have been developed with suitable curing characteristics and mechanical properties. Soy resins have been commercialised by a number of companies, most notably Urethane Soy Systems (US) who supply a soy-based polyurethane called SoyMatrix™.

Cambridge Biopolymers (UK) transforms plant oils to resin precursors that can be polymerised by a catalyst and heat. Their patented technology involves using the reactivity of ozone to attack the double bonds of the oil, thereby forming oxygen linkages that can be converted into cross-linkable units. The resins can be used as sustainable alternatives to petrochemical-based urea and phenol formaldehydes and isocyanates, which are hazardous to health, for example in wood-based products such as MDF. Sustainable Composites (UK) produces a resin called EcoComp® UV-L, which is reported to contain 95% vegetable oil and is cured by ultraviolet light sources. Perceived advantages include no VOCs or harmful solvents, extended working time and curing time as little as 3 to 6 minutes.

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Figure 11: Cashew nut shell liquid based Flax Coral Prepreg, produced by CTS, Ohio. Photo courtesy of Elmira Ltd, UK.

Cashew Nut Shell Liquid (CNSL) is another natural oil which can be successfully converted into thermosetting resins. Cardanol is an alkyl-phenolic product obtained by vacuum distillation of CNSL which is reactive thanks to double bonds in the alkyl chain and the phenolic character [59]. Large quantities of cashew nuts are produced in Africa, India and Brazil, which means that the price of CNSL is lower than similar synthetic phenolics, although its composition is significantly more variable. CNSL-based polymers are under development by a number of companies, such as Cardolite in the USA and Elmira in UK (working with sister company Composite Technical Services in USA) and various companies in India. Elmira has developed part bio-based epoxies and urethanes for composite processes, and can supply novolacs and polyols based on CNSL.

3.2.2 POLYFURFURYL ALCOHOL

Polyfurfuryl alcohol (PFA) resins are a family of thermosetting bioresins derived from furfuryl alcohol, a renewable alcohol produced from furfural, which is formed by the acid catalyzed digestion of hemi-cellulosic sugars in biomass. Suitable feedstock materials are agricultural wastes, with the most common being sugar cane bagasse. Furfuryl alcohol and related PFA resins are widely used in the foundry industry as a binder for sand and refractory products. The properties of these resins, which include high levels of thermal stability, chemical resistance and fire retardance, are particularly attractive to the composites industry. A leading manufacturer of PFA resins is TransFurans Chemicals (Belgium), who supply a range of resins, under the trade names Biorez and Furolite, for different composite processes including hand lay-up, RTM, BMC/SMC and prepregs [60].

3.3 SYNTHETIC-BIO-BASED POLYMER BLENDS

Whilst the general aim in bio-based polymer development is to produce polymers derived entirely from renewable sources, this is not always realistic particularly in the short term. For example, where the renewable materials are currently significantly more expensive than their synthetic alternative or where the properties of a 100% bio-based system are inferior, it is often a better option to use a resin made from a mixture of synthetic and bio-based chemicals.

For example, DuPont's Sorona polymer, which is a polytrimethylene terephthalate (PTT), is based on Tate & Lyle's propanediol (PDO) derived from corn sugar. Sorona

contains 20-37 weight% renewably sourced ingredients and reportedly reduces energy use by 30% and greenhouse gas emissions by 63% during its production. The material is thought to exhibit performance and moulding characteristics similar to polybutylene terephthalate (PBT) and is used in carpets, fabrics and plastic mouldings.

Ashland supplies a range of part-renewable unsaturated polyester resins under the ENVIREZ® trade name. The renewable content of these resins is around 10-20% and is also based on Tate & Lyle's PDO material. Resins are available for a range of composite processes including hand lay-up, RTM, SMC and pultrusion. Other partially bio-based polyester resins include DSM's Palapreg Eco (55% bio-based content), CCP Composite's Enviroguard (20-50% bio-based content) and Reichhold's Envirolite (25% bio-based content.

There are a number of epoxy resins on the market which contain a proportion of bio-based material. Entropy Resins produce SuperSap which contain about 15% bio-based content, whilst Sicomin's Greenpoxy claims a bio-based content of over 50%. Dragonkraft have produced a range of bio-based epoxy resins and hardeners. The resins are 97-100% bio-based whilst the hardener has about 20% bio-based content. Details of how the resins are made are not disclosed but they do state that the products are free from bisphenol-A and amines.

Bio-based polyamides are also available such as EcoPaXX polyamide 410 from DSM which is based on castor oil and contains 70% renewable content. Arkema produce Rilsan ® PA11 which is also based on castor oil but is described as being 100% renewable origin.

Further examples include thermoplastic elastomers from Merquinsa (Pearlthane Eco D12T90).

It is also possible to use bio-based products to improve the performance of synthetic resins. For example, the impact strength of petroleum-based epoxies can be significantly improved by blending with epoxidised vegetable oils [34].

3.4 PROPERTIES

As with petrochemical-based polymers, bio-based polymers exhibit a wide range of properties from rigid and brittle to flexible and tough. Table 3 summarises some properties of selected bio-based polymers. Polyester-type bio-based polymers such as PLA and PHB tend to have the highest tensile modulus and tensile strength, while plasticised starch and PHBV copolymers tend to have higher elongation. Impact modifiers are commonly used to improve the toughness of PLA and a typical product is DuPont Biomax® Strong 100 or 120, which is an ethylene copolymer. Products are also available to improve the thermal stability of PLA such as DuPont Biomax® Thermal 300.

Thermosetting bioresins are generally considered to be non-biodegradable, although data is scarce on this subject.

GRADE	POLYMER	DENSITY (g/cm³)	MELT FLOW INDEX (g/10 min)	MELTING TEMPER-ATURE (°C)	TENSILE MODULUS (GPa)	TENSILE STRENGTH (MPa)	TENSILE ELONG-ATION (%)	IZOD IMPACT, NOTCHED (J/m)
EcoDear	PLA	1.11	16	150-175		52	10	8.8
Biomer P266	PHB	1.25	10	40-180	1.9	25	6-9	2.7
Plasticised starch acetate [50]	Starch	1.28		<170	0.61	10.3		8
Novamont Mater-Bi AB 05 H	Starch & polyester	1.28	3	146	1.1	19	160	
Soy bioplastic [34]	Soy				0.2	8.5		32.9
Triglyceride polymers [58]	Triglyceride				1.6-2.5	21-44	3.8-5.2	

Table 2: Properties of bio-based polymers.

4 BIO-BASED CORE MATERIALS

Lightweight core materials, such as honeycombs and foams, are often integrated within composite structures as a means of significantly increasing flexural stiffness for a small increase in weight. For the biocomposite designer, there are several bio-core options available. Some are well-established and have been used in conventional composite structures for many years (e.g. balsa wood), whilst others are emerging technologies that are still being proven in widespread application.

BALTEK® SB balsa wood from controlled cultivation, cut perpendicular to the grain direction for optimum properties. Photo courtesy of Airex AG.

4.1 CORES FROM TREES

Balsa wood is a lightweight material with many uses, including as a core for composite sandwich structures. When used as a sandwich core, it is kiln dried (to remove the water contained in its large cells) and used in an "end-grain" configuration (i.e. with the grain of the balsa wood running through the thickness of the core). A range of different densities are available, 100-250 kg/m3 for composite applications. As a composite core material, it tends to be somewhat more dense than many honeycombs and polymer foams, but it provides good strength and stiffness, and excellent impact/indentation resistance. Its fire resistance is superior to polymer foams core materials hence its use in naval and other marine structures over many years.

Cork is widely used for bottle stoppers, but the trend towards screw caps and synthetic stopper materials has encouraged the industry to seek new applications for their product. Cork crumb is made by granulating the bark after the stoppers have been removed. This is then bonded, typically using a polyurethane adhesive, to form sheets (Figure 11). The density of these sheets is 120-250 kg/m3, although it is possible to make sheets with a higher density. Cork has excellent thermal insulation and damping properties. It is renewable; the bark is stripped from a cork oak once every 9 years.

4.2 BIO-BASED POLYMER HONEYCOMBS

Honeycomb geometries can provide very efficient and lightweight sandwich cores. They are most often produced from aluminium foils, resin-coated paper or cardboard, but they can in theory be made from many sheet materials, including bio-based polymers. For example, EconCore N.V. market a honeycomb core that is produced from a 100% bio-based PLA polymer [61]. Its upper temperature range is rather low at only 55oC, but it is an interesting product nonetheless.

Paper and cardboard honeycombs are, of course, also bio-based, although their susceptibility to moisture can be barrier to their use in many applications.

Figure 12: Granulated cork formed into a sheet, courtesy of Amorim Cork Composites.

4.3 BIO-BASED POLYMER FOAMS

Polymer foams are also widely used as composite sandwich cores, with the common incumbent materials including polyurethane, polyvinyl chloride and polyetherimide. Various attempts have been made to produce foams based on bio-based polymers, including those derived from starch [62], PLA [63], tannin [64,65] and flax oil [66]. However, in terms of their suitability for use as structural sandwich cores, these bio-based polymer foams are typically compromised in one or more respects (e.g. low mechanical properties, brittleness, or low temperature resistance). This doesn't preclude their use in other application areas, for example as packaging materials or thermal insulation.

4.4 NANO CELLULOSE FOAMS

Cellulose, the primary structural component of plants, is the most ubiquitous and abundant organic compound on the planet. Through careful processing it is possible to extract nano-fibrils or nano-crystals from cellulose, and then assemble these nano particles into cellular, foam-like structures [67]. The technology is still in its relative infancy, but promising nonetheless. For example, the NCC-FOAM project [68] is up-scaling the production of nano-crystalline cellulose foams for composite sandwich applications based on the technology of Melodea.

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4.5 PROPERTIES

Table 3 shows some typical material property data for a range of bio-based core materials. In general, the properties of cellular materials are very dependent on their density, hence the relatively wide range of values.

MATERIAL	DENSITY (g/cm³)	COMPRESSIVE MODULUS	TENSILE STRENGTH (MPa)	ELONGATION TO FAILURE (%)	MOISTURE ABSORPTION (%)
Balsa wood[69]	0.1 – 0.25	2000 - 8000	5 - 25	100 - 300	2 - 5
PLA honeycomb (THPLA80) [61]	0.08	40	1.1	-	-
PLA Foam [63]	0.04	-	0.2	-	-
Tannin foam [64,65]	0.05 – 0.15	-	0.2 – 1.3	-	-
Cork [70]	0.14 – 0.25	5-7	0.3-0.6	6	130-145

Table 3: Mechanical properties of bio-based materials used as cores in composite panels.

5 NATURAL FIBRE-SYNTHETIC POLYMER COMPOSITES

5.1
WOOD PLASTIC COMPOSITES

Wood Plastic Composites (WPCs), also called plastic lumber, consist of short wood fibres (<1 mm long) or wood flour in thermoplastic polymer matrices, most commonly polypropylene (PP), polyethylene (PE) and poly vinyl chloride (PVC). These polymers are chosen due to their low cost and low processing temperature, which minimises degradation of the wood fibres. In many cases, the matrix is a recycled polymer due to the relatively low technical and aesthetic demands. Wood flour is an attractive feedstock because it has high bulk density, it is free-flowing during processing and, due to being a waste product from sawmills, has low cost and high availability. The wood content of WPCs is typically 30-70% by weight and commonly used wood types are fir, pine, spruce, maple, oak and beech.

The materials are compounded in an extruder, typically a twin-screw extruder although some benefits have been noted when using planetary extruders, and then chopped into pellets suitable for extrusion or injection moulding. It is also possible to extrude directly into the desired profile, and to thermoform parts from extruded sheets. The wood fibres must be dried to <0.5% by weight of water to ensure a good finish and the extruder typically needs vacuum venting to remove any residual moisture [71]. During the compounding stage, it is normal to include other processing aids or functional additives such as lubricants, coupling agents, dispersing agents, foaming agents, antioxidants, thermal stabilisers, impact modifiers, UV stabilisers, pigments and fungicides.

WPCs typically have good stiffness, strength and heat resistance but low impact strength. Impact strength can be improved by adding modifiers such as 1 weight% maleic anhydride PP (MAPP), 2 weight% ethylene-propylene-diene monomer (EPDM) or viscose fibres (e.g. 10 weight%) [71]. WPCs also exhibit low in-mould shrinkage. Typical properties are shown in Table 4.

The most important applications for WPCs are in construction (decking, railings, outdoor furniture, picnic tables, garden benches etc.), automotive (door liners, parcel shelves, enclosures, loudspeaker housings etc.), industrial goods (pallets, boards) and consumer goods (furniture, flower pots, tableware, handles etc.).

Not all plastic lumber includes wood fibres. In the UK, plastic lumber is also manufactured from pure mixed polyolefins, sometimes with the addition of some polystyrene to improve properties, or thermoplastics with glass or flax reinforcement.

	TENSILE MODULUS (GPa)	TENSILE STRENGTH (MPa)	IMPACT STRENGTH (J/m²)	HDT (°C)
WPC 30% [44]	3.2-3.8	28-32	11-13	74-94
WPC 50% [44]	28-32	11-13	74-94	2 - 5

Table 4: Typical properties of WPCs.

5.2
NATURAL FIBRE INJECTION MOULDING COMPOUNDS

In distinction from WPCs, this section will consider synthetic thermoplastic polymers reinforced with natural fibres typically 1 mm in length or greater. The vast range of different natural fibres and thermoplastic matrices available and combinations investigated make it difficult to write a meaningful summary. Therefore, this section will only focus on the most widely used materials and processes.

An important family of biomaterials are short natural fibre-thermoplastic injection/extrusion moulding compounds. These are most commonly hemp-PP, although flax and jute are also used, the natural fibre content is typically 20-50% and the fibre length is typically 1-10 mm. The materials are compounded in a similar way to WPCs, typically using twin screw extruders, and controlling the temperature to avoid degradation of the natural fibres. It can be difficult to dose loose fibres accurately during the process so one possibility is to pelletise the fibres prior to compounding.

MATERIAL	DENSITY (g/cm³)	TENSILE MODULUS (GPa)	TENSILE STRENGTH (MPa)	ELONG-ATION (%)	CHARPY IMPACT STRENGTH (J/m²)
PP-30% jute [73]		4.6	36-50		27-28
PP-50% jute [73]		8.6	36-65		32-33
PP-35wt% jute [74]		4	76	4	16
PP-50wt% jute [74]		5.3	87	3.2	14
PP-45% jute [75]	1.08	5.1	54	2.3	19
PP-30% flax [75]	0.99	4.2	52	2.5	17
PP-30% hemp [75]	0.99	4	44	3.8	18.2
PP copolymer-50wt% kenaf [76]	1.07	7.5	53	2.5	-

Table 5: Typical properties of short natural fibre-thermoplastic composites.

As outlined in section 2.5, natural fibres tend to bond poorly to polymers but adhesion can be improved by using compatibilisers. By far the most commonly used compatibiliser for PP-NF is maleic anhydride-grafted polypropylene (MAPP) and numerous studies have reported successful results. For example, the tensile strength of PP-50% jute can be increased from 36 to 65 MPa with just 1% addition of MAPP, whilst the modulus is unaffected and impact strength only slightly reduced [73].

PP-NF materials tend to have good stiffness and strength, low shrinkage, good acoustic properties and provide significant weight savings. Selected properties are summarised in Table 5 and indicative prices against competing materials are shown in Figure 12. They have the potential to replace some engineering polymers or glass / talc filled PP. Typical applications of short natural fibre-PP compounds are automotive parts (trim parts, dashboard parts, glove box) and consumer goods (electrical goods, rigid packaging, plant pots, mobile phones).

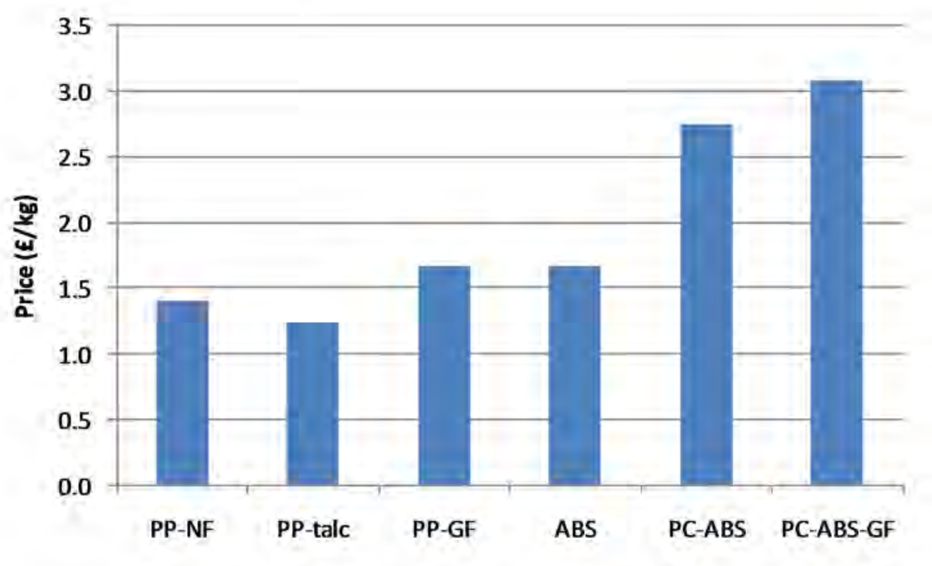

Figure 13: Indicative prices of PP-NF granules and competing injection moulding materials. Data from [75].

5.3 NON-WOVEN NATURAL FIBRE MAT COMPOSITES

One of the most significant applications for natural fibres is press-moulded automotive parts, where weight savings of 30% are possible [72]. For this application, the natural fibres, commonly flax, hemp or kenaf, are carded and needle-punched to produce non-woven mats or fleeces. Typically, the natural fibres are either pre-blended with thermoplastic fibres, usually PP, or sprayed with a thermosetting resin, usually polyurethane (PU) or epoxy, so that the mats contain an even distribution of both fibre and matrix components. The thermoplastic variant is sometimes referred to as natural fibre mat-thermoplastic (NMT).

The mats are then heated to the melting temperature of the PP binder or the curing temperature of the PU and pressed into shapes, which tend to be relatively simple due to the limitations of the process. It is possible to incorporate fixings and coverings in a one-shot process, the parts have good mechanical properties, low shrinkage, high noise absorption, low odour and are recyclable (e.g. can be converted to granules). Currently EcoTechnilin produce needle-punched mats consisting of natural fibres and thermoplastic fibres and FibriBoard which is a preconsolidated sheet of the same. They also have fully bio-based versions – see section 6.2. Dräxlmeier also produce natural fibre (kenaf)-polypropylene sheets with a non-woven core and a skin of polypropylene film. This gives a final structure consisting of well consolidated skins and a core of less consolidated material. An independent study showed that this provides an optimum balance of density, stiffness and impact strength [77]. The main applications are interior trim including door liners, boot liners, parcel shelves, headliners, seat backs, pillar trim and centre consoles.

Another use of non-woven natural fibres mats is in thermoset composite production using conventional resins such as polyester, vinyl ester and epoxy. Non-woven natural fibre mats lend themselves to resin infusion and injection type processes, such as resin transfer moulding (RTM) and vacuum assisted RTM (VARTM) and can be an environmentally friendly substitute for glass chopped strand mats and continuous filament mats. The mats must not be too dense because resin flow can be restricted, although some commercial products are supplied with a flow core inside to improve this. The natural fibres may need to be dried prior to moulding to prevent problems with resin cure and compatibility. Chemical modification of the fibres can aid adhesion, for example esterification of hemp hydroxyl groups using methacrylic anhydride [78], although adhesion is considered to be less of an issue for thermoset resins than thermoplastics. Processing issues such as fibre 'washing' and preferential edge flow, which can also be problems for glass fibre mats, have been noted during injection of hemp mats [79]. These can be alleviated by manipulation of the reinforcement to achieve steady state flow.

Applications for natural fibre-thermoset RTM parts include automotive (e.g. exterior and interior panels for cars, trucks, caravans etc.), marine (exterior and interior walls, decks, structures), construction (panels, cladding) and industrial (covers, tanks).

MATERIAL	DENSITY (g/cm³)	TENSILE MODULUS (GPa)	TENSILE STRENGTH (MPa)	ELONGATION (%)	IMPACT STRENGTH (kJ/mm²)
PP-30wt% jute [80]	1.09	7.8	68.1	1.5	
PU-25vol% NF [81]	1.25	6.5	75	1.6	
PU-35wt% NF [7]	1.42	6	70	1.9	20

Table 6: Properties of non-woven natural fibre mat composites.

5.4
ALIGNED NATURAL FIBRE-REINFORCED COMPOSITES

Natural fibres, by their nature, are discontinuous and after processing they are usually in a randomly oriented state. As discussed in section 2.3.3, much higher composite strength and stiffness can be achieved by using continuous, aligned fibre reinforcements. Aligned natural fibre composites have not been studied to a great extent at least in part due to the lack of availability of suitable reinforcement yarns and fabrics. However, studies that have been carried out in this area, most notably at Risø National Laboratory (Denmark), have shown that outstanding mechanical properties can be achieved through using aligned flax and hemp (Table 7).

Aligned natural fibres can be combined with thermoplastic polymers in a number of ways. Woven or stitched fabrics can be interleaved with thermoplastic sheets or films, often referred to as film stacking, then heated and consolidated in a press or by vacuum bagging [82]. In lab-based trials, natural fibres yarns can be wound onto a frame to make pseudo-unidirectional reinforcements, then interleaved with thermoplastic films or sheets, or co-wound with thermoplastic yarns, prior to heating and pressing [33]. In all cases it is necessary to limit the temperature and time at temperature to prevent degradation of the natural fibres. Some benefit has been noted by heating under vacuum to reduced oxidation effects. Natural fibre-thermoplastic pultrusion is also possible [83], although the natural fibre materials must have sufficient strength to resist breaking during the process. Thermoplastic polymers are highly viscous so do not flow readily and care must be taken during processing, as with all thermoplastic composites, to ensure good impregnation and consolidation.

Aligned natural fibre-thermoset composites can be produced using standard processes such as hand lay-up, RTM, pultrusion and filament winding. Again, it is often necessary to dry the natural fibres before processing.

MATERIAL	DENSITY (g/cm³)	TENSILE MODULUS (GPa)	TENSILE STRENGTH (MPa)	ELONGATION (%)
PP-42vol% flax [33]		26.9	251	1.5
PET-31vol% hemp [33]		20.1	221	1.8
UP-37vol% flax [77]	1.42	24	248	1.5

Table 7: Properties of aligned natural fibre composites.

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6
FULLY BIO-BASED COMPOSITES

Fully bio-based composites, where both fibre and matrix are naturally sourced, continue to emerge. A considerable amount of research effort has been and is being conducted in this area and, indeed, there are examples of commercial developments.

6.1 NATURAL FIBRE-BIO-BASED POLYMER INJECTION MOULDING COMPOUNDS

Natural fibre-bio-based polymer compounds, suitable for injection moulding and extrusion, have been under development for a number of years. In particular, the continuous progress and improvement in thermoplastic bio-based polymers such as PLA, starch and lignin, coupled with the need for increased stiffness and thermal stability, have driven the development of natural fibre-reinforced compounds.

The recent European project BIOCOMP developed injection moulding and extrusion compounds and process methods for bio-based composites based on wood, flax and hemp fibres and PLA, starch and lignin matrices [84]. The ideal process for compounding PLA-flax is to use a co-rotating twin screw extruder with 180 °C barrel temperature, 43 bar pressure at the die and a vacuum vent for removing residual moisture. Some benefits can be obtained by using a planetary screw extruder, although these machines are relatively rare. Pelletised fibres are easier to feed than loose fibres. The inclusion of natural fibres reduces the impact strength of the PLA compounds and impact modifiers are therefore required to regain the impact strength. The injection moulding process has also been optimised and a range of demonstrator products have been produced including corner protectors, boxes and industrial platform tiles. Compounds and processes for extrusion of PLA-flax have also been developed, optimised and demonstrated by producing a hollow decking profile.

Starch-based compounds have been developed containing 50% natural fibre (hemp, flax or wood) for injection moulding and 60-70% for extrusion. The most suitable starch is a high amylose grade which is then plasticised with 20-35% triethyl citrate (TEC) before being compounded with the natural fibres in a co-rotating twin screw extruder at 200 °C. For injection moulding, the optimum process parameters are 180-200 °C melt, 50 bar pressure, 100-180 mm/s injection speed and 25-30 °C mould temperature. For extrusion, the most suitable parameters are 180-200 °C at the screw and 150-170 °C at the nozzle [50].

Lignin-natural fibre compounds have been developed with 10-45% natural fibre content, using a pelletising process which effectively presses the lignin powder and natural fibres together into agglomerates. The compounds can be injection moulded at 140-160 °C to produce complex parts with properties and appearance similar to wood. Fire retardance up to UL94V-0 standard can be achieved through the addition of <10% fire retardant additive. Due to their outstanding acoustic properties, lignin-natural fibre materials are particularly suitable for loudspeaker housings, musical instruments, etc. This material is now commercially available from Tecnaro (Germany) with the trade name Arboform®.

MATERIAL	TENSILE MODULUS (GPa)	TENSILE STRENGTH (MPa)	ELONGATION (%)	CHARPY IMPACT STRENGTH (kJ/m²)
PLA-NF	4-7.5			12-19
PLA-NF-IM	3.2-6.2			20-31
PLA-30wt% kenaf [76]	7	65	1	
PLA-30% flax [7]	8.3	53	1	
PLA-40% flax [34]	7.2	68		
Starch- 30% FEC-40% flax	8.1	50.7		5.2

Table 8: Properties of natural fibre-bio-based polymer compounds.

Within the same project, higher performance PLA-flax materials have been developed using the direct-long fibre thermoplastic (D-LFT) process [22]. This process involves compounding the PLA granules with the desired additives (e.g. impact modifier) in a single screw extruder, which feeds into a twin screw extruder where it is compounded with the flax fibres (chopped fibre or carded slivers), extruded as a hot dough, transferred to a press and compression moulded. A suitable impact modifier was found to be BASF Ecovio® LBX 8145 and regenerated cellulosic fibres were identified as a possible route to improve toughness further. The biocomposite D-LFT process was demonstrated by producing an automotive foot rest.

Typical properties of natural fibre-bio-based polymer compounds are summarised in Table 8.

6.2 NON-WOVEN NATURAL FIBRE-BIO-BASED POLYMER COMPOSITES

Analogous to the materials described in section 4.3, non-woven natural fibre mats can be produced with thermoplastic bio-based polymer or thermoset bioresin binders. Typical properties of these materials are shown in Table 9. In particular, Toyota have developed automotive parts from press moulded kenaf-PLA non-woven mats, including the Toyota Raum spare wheel cover, which is claimed to be the first 100% natural automotive product in the world [85]. In the UK, EcoTechnilin's FibriPlast product can be made with PLA fibre.

MATERIAL	TENSILE MODULUS (GPa)	TENSILE STRENGTH (MPa)	CHARPY IMPACT STRENGTH (kJ/m²)
PLA-50% flax [34]	6	99	14.3
PLLA-40% jute [34]	9.4	100	

Table 9: Typical properties of natural fibre-bio-based polymer non-woven mats.

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6.3 ALIGNED NATURAL FIBRE-BIO-BASED POLYMER COMPOSITES

As discussed in section 2.3.4, aligned fibres such as those in woven or multi-axial fabrics offer improved mechanical properties over short, randomly oriented fibres like those in non-woven mats. The Biotex family of materials supplied by Composites Evolution (UK) includes a range of aligned, commingled flax/PLA yarns, fabrics and preconsolidated sheets which are fully bio-based and biodegradable and provide good stiffness, strength and processing characteristics.

Figure 14: Automotive door panel made from non-woven natural fibre mat with furan bioresin (photo used with kind permission of TransFurans Chemicals).

6.4 NATURAL FIBRE-THERMOSET BIORESIN COMPOSITES

A number of research and development studies have been conducted in the area of natural fibre-thermoset bioresin composites. Perhaps most notable is the Affordable Composites from Renewable Sources (ACRES) programme at the University of Delaware (USA), which has combined the soybean resin derivatives, described in section 3.2, with flax, hemp and jute fibres to produce biocomposites for applications including chairs, hurricane-resistant houses and automotive body panels [58]. Soybean-natural fibre composites have been used commercially by John Deere, under the trade name HarvestForm®, to produce body panels and cab roofs for hay balers. The parts are produced by the RIM process and 25% weight savings are claimed.

In the UK, the University of Warwick have developed natural fibre-vegetable oil composites for the body panels of their Eco One and WorldF3rst sustainable racing cars [86] and a team of companies including the Eden Project, Homeblown, Sustainable Composites and Laminations have developed a surfboard comprising natural fibre-bioresin skins with a biofoam core.

The European BIOCOMP project developed thermosetting biocomposites, including flax fibre-polyfurfuryl alcohol (PFA) bioresin and wood fibre-linseed oil resin [84]. A range of PFA bioresins have been developed by TransFurans Chemicals (Belgium) for different composite processes including press moulding, BMC/SMC and prepreg. For press moulding, the furan resin is sprayed onto non-woven natural fibre mats and then hot press moulded at 180 ^{o}C for <60 s. This system has been successfully applied in the manufacture of prototype automotive door panels (Figure 14) and passes all the required tests and specifications [60]. Bio-based BMC/SMC materials have been developed from furan bioresin and natural fibres by Gaiker (Spain). The compounds can be hot compression moulded in a similar fashion to conventional BMC/SMC materials and have good fire-retardant characteristics, making them suitable for applications in the electrical and automotive sectors.

NetComposites has developed a range of bio-based prepregs based on natural fibre textiles and a polyfurfuryl alcohol (PFA) resin which can then be processed into composite parts by vacuum, autoclave or press consolidation. By using aligned natural fibres, the mechanical properties of these biocomposites are significantly higher than non-woven mat composites [87]. These PFA prepregs are now commercially available through Composites Evolution Ltd [88] (Figure 13, Table 10) and provide a more sustainable alternative to glass-phenolic prepregs.

PROPERTY	VALUE
Density	1.450 g/cm^3
Flexural Strength	109 MPa
Flexural Modulus	8.5 GPa
Tensile Strength	69 MPa
Tensile Modulus	10.5 GPa

Table 10: Typical properties for the EcoPreg material, courtesy of Composites Evolution Ltd.

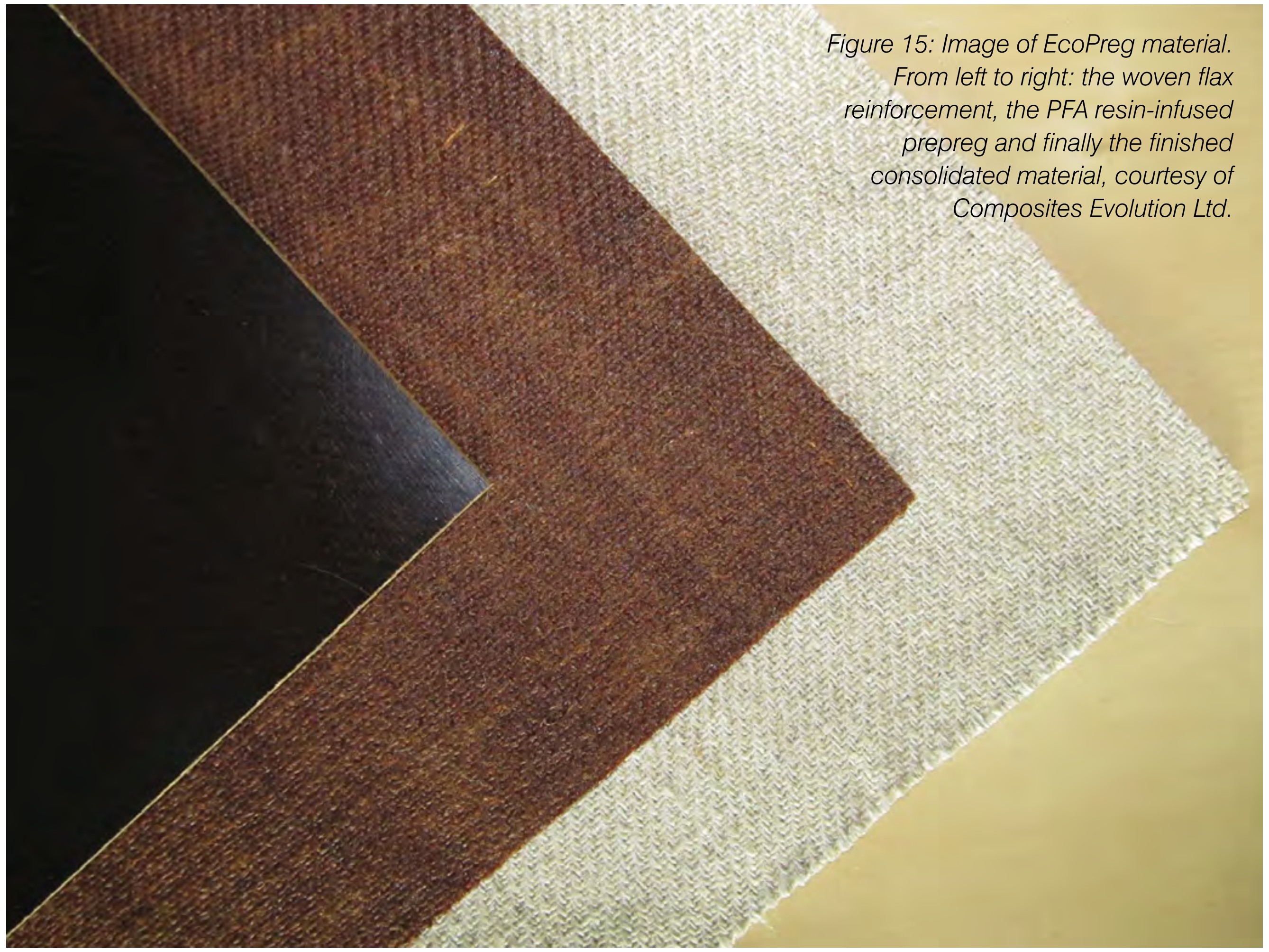

Figure 15: Image of EcoPreg material. From left to right: the woven flax reinforcement, the PFA resin-infused prepreg and finally the finished consolidated material, courtesy of Composites Evolution Ltd.

As discussed in section 3.2, one of the main drivers of the development of thermoset bioresins is the need to find less hazardous alternatives to binders such as urea and phenol formaldehyde for wood products. As such, a number of studies have been conducted in this area [89]. In particular, Chemont (Belgium) have developed a linseed oil resin which can be used as a binder in wood products such as MDF [90].

Example properties of natural fibre-bioresin composites are summarised in Table 11.

MATERIAL	DENSITY (g/cm³)	TENSILE MODULUS (GPa)	TENSILE STRENGTH (MPa)	ELONGATION (%)	IMPACT STRENGTH (kJ/m²)
PFA-natural fibre mat	0.8-0.85	3-5.5	30-40	1-2	>10
PFA 40 vol% biaxial flax	1.35	9.6	99.4	1.2	12.5
Linseed oil resin-wood	1.1		25-40		

Table 11: Properties of natural fibre-bioresin composites.

6.5 FUTURE DEVELOPMENTS

Future developments in fully bio-based composites are likely to be controlled, at least in part, by the speed of development in natural fibres and bio-based polymers. As discussed previously, consistent quality natural fibre products are required in appropriate forms for composite moulding and at an affordable price. To achieve this, improvements in crop growing and fibre processing are required, an area being investigated in the UK by DeMontfort University in particular.
The development of aligned natural fibre materials suitable for composite reinforcement will be important if biocomposites are to be used in more demanding, load-bearing applications. The UK-based COMBINE project developed high performance aligned natural fibre fabrics for composites [24]. The European project, NATEX developed a range of textiles based on aligned natural fibres and investigated methods by which these could be converted into composite articles. Both thermoset and thermoplastic resins were used.

Bio-based polymers and bioresins with improved processing characteristics and properties are required if the materials are to be widely adopted. In particular, ways of improving the thermal stability and toughness of bio-based polymers such as PLA and PHB are under investigation. There is great market demand for thermosetting bioresins and significant efforts are being made to produce resins with high renewable content and suitable viscosity and curing characteristics. In particular, bioresins with low viscosity and low curing temperature are required for conventional composite processes such as hand lay-up and RTM. In the short term, hybrid resins with a smaller proportion of renewable content may be the best option.

In some cases, the compatibility of natural fibres and polymers needs to be improved, for example by developing suitable fibre treatments, modifying the polymers or a combination of both.

7 ENVIRONMENTAL ISSUES

Products made from composite materials can offer significant environmental benefits because of their characteristically low weight, good mechanical properties, excellent resistance to corrosion and the possibility of being sustainably sourced. For example, composites used in cars can reduce the overall weight of the car and so offer fuel savings through the lifetime of the vehicle. However, although the in-service environmental benefits of composites are known, there is far less understanding of the environmental and social implications associated with the manufacture of composite materials and products, and the options at end-of-life.

Issues affecting the composites industry include health and safety, the emission of volatile organic compounds (VOCs), energy consumption and toxicity from manufacture. Natural materials and technologies have been developed, in part, to help address these problems, but to date there has still been confusion within the industry as to the detailed benefits of these alternatives. Generally, naturally-derived fibres and polymers are perceived as being ‘greener’ than their synthetic alternatives, but in some instances this has been proven to not be the case. For example, in instances where a certain stiffness of component is required, Life Cycle Assessment (LCA) methods have shown that a composite of natural fibres in a synthetic resin is less competitive than a carbon-fibre equivalent, as the component has to be thicker to achieve the same performance and therefore uses more resin. The use of composites in automotive applications is another very good example, where the reduced weight possible by using composites is offset by reduced recyclability compared to steel [91].

Work is ongoing to establish the environmental credentials of naturally derived products in order to enable designers to assess and exploit their environmental benefits where appropriate. Initiatives such as PAS 600:2013 [1] and the Inventory of Carbon and Energy (ICE) [92] aim to give more consistent and accurate information.

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7.1 LIFE CYCLE ASSESSMENT

When measuring environmental impact it is important to consider all the influences through the life of the product using a process known as Life Cycle Assessment (LCA). This is a modelling system which enables the quantification and validation of these impacts, taking into account social, environmental and economic factors. It can also be used to directly compare different materials and processing routes.

Cradle-to-gate methodology assesses the impacts associated with the extraction of oil, minerals and biomass as precursors to the resin and fibre, the manufacture of the materials, any requirements for transport or packaging and finally the composite manufacturing process itself. The use of the product beyond the factory gate can have a significant effect on the overall environmental impact of the part and so a more rounded approach is the cradle-to-grave assessment, which looks at a product from its manufacture to its use, and finally to end-of-life and disposal. This allows designers to see how they can use composites to benefit the environmental credentials of their products.

Within the LCA model, a range of impacts are listed, including human toxicity, eutrophication, carbon sequestration, ozone depletion and acidification. These are given different weightings depending on their severity to human survival (minor variations in the weightings given to such impacts are common between LCA models). LCA begins with building an environmental profile using raw data on the material, product or process of interest. Raw data on all works inputs, outputs, direct consumption of fuel, and wastes are collected from the manufacturing site. The raw data is normalised and modelled according to the weighting system. An eco point rating is then assigned to the activity per unit weight. To enable direct comparison between different materials, functional units are modelled, whereby a product's primary function or use is defined and the quantity of materials required during its production are calculated. The particular eco points given to each material can then be used comparatively.

LCA standards are in continuous development, but PAS 2050:2011 (Specification for the assessment of the life cycle greenhouse gas emissions of goods and services) has been introduced to provide an internationally applicable method for quantifying product carbon footprints [93]. The GHG Protocol Product Standard, released about the same time, provides methods to quantify Green House Gases and the requirements for public reporting [94]. Both documents are largely consistent in their approach, although they deal with different aspects of environmental impact.

The IS014000 family of standards address various aspects of environmental management and provides tools for organisations to identify and control their own environmental impact [95].

7.1.1 ENVIRONMENTAL IMPACT OF NATURAL FIBRES

The production of fibre crops has varying impact on the environment as far as the requirements for fertiliser and pesticides, water and energy are concerned. In general, fibre crops are found to have moderate requirements for fertiliser and crop protection chemicals, whilst energy requirements can be thought of as very small due to the extensive farm structure and the relative importance of labour in traditional farming systems. Consequently, the production of fibre crops has a limited impact on the environment [96].

In a study comparing the environmental impact of different natural fibre retting processes (scutching of green hemp followed by water retting, retting of premature hemp and dew retting of flax) neither process was found to be significantly better than the reference process which was warm water retting of hemp [15]. Pesticide use was higher for flax and water use was higher for hemp. Scutching of green hemp followed by water retting had a higher energy input during processing. Premature hemp had higher impacts for eutrophication, land use and pesticide use.

In the post-harvest processing steps, the fibre extraction process consumes fossil energy and water, generates biomass waste and contaminates process water. The latter presents a risk of pollution of surface waters if no measures are taken for waste water treatment. Utilisation of residues and waste for generation of energy, or other value added outlets, substantially enhances the overall ecological performance of a fibre crop. In general, comparative studies on the production phase of fibre crops with synthetic products, or glass fibres, indicate that fibre crops provide environmental benefits in terms of reduced CO_2 and greenhouse gas emission levels and consumption of fossil energy.

In general, most of the environmental benefits of fibre products accrue during the utilisation phase. The weight reduction of natural fibre composites in automotive applications contributes more to the protection of the environment in terms of fuel savings than energy savings in the production phase of the part. However, as highlighted before, end-of-life options could render steel an overall more environmentally friendly choice. When the same mechanical strength is desired, the advantage of using lignocellulosic fibres over glass fibres in a composite may be lost because heavier constructive elements are required. However, when the same stiffness is required, lignocellulosic fibre can give lighter constructive elements, due to their higher specific stiffness. Nevertheless, it is important to note that the magnitude of the environmental advantages depend on the kind of application. The predominant environmental gain is usually due to a secondary effect, such as weight saving, rather than the bio-based origin of the fibre.

7.1.2 ENVIRONMENTAL IMPACT OF BIO-BASED POLYMERS

The environmental impact biopolymers depends on the source of the chemical feedstock and the application. End of life options can be significant in a full LCA, and sourcing feedstock from waste is generally advantageous.

A study commissioned by Natureworks, which compared the environmental impact of thermoformed 'clam shell' food packaging, found that PLA scored well compared with PET, PS and PP [97]. Lighter-weight parts were possible due to the stiffness of PLA and the end-of-life options for PLA were better than for PET. Interestingly, however, recycling of PLA was a more favourable end-of-life option compared to composting. The environmental indicator with the highest relative contribution for PLA production was aquatic eutrophication, mainly caused by chemical oxygen demand (COD), a measure of organic compounds emitted from the PLA production system, and nitrate emissions from corn growing.

A recent critical review looking at discrepancies between life cycle assessments of biodegradable biopolymers was undertaken by University of Cambridge [98]. Focusing on poly(lactic acid) (PLA), poly(hydroxyalkanoates) (PHAs), and starch-based polymers, this attempted to determine the environmental impact of each in comparison to petrochemical polymers, taking into account the farming practices involved which can carry significant environmental burdens. It was found that many studies focused on energy and global warming potential and found in favour of biopolymers, but those which considered other environmental impact categories or were regional / product specific were not so favourable. However it notes that the immature nature of these technologies needs to be taken into account as future optimization and improvements in process efficiencies are expected.

A LCA on multilayer packaging films, conducted as part of the European project Multibio, found that a bio-based polymer film made from modified starch and PLA had nearly half the environmental impact of a conventional film based on PP and PA6 [99]. The bio-based polymer film performed particularly well in the area of global warming, which was the most significant impact category. The bio-based polymer film had lower fossil energy depletion impact than the conventional film but differences in the acidification category were small. In the area of eutrophication, the bio-based film performed less well, although this category was found to contribute the least environmental impact overall.

Use of waste biomass, from agriculture, food or animal waste, is of considerable interest for resin feedstock. One recent study of cradle-to-gate production of polyhydroxybutyrate (PHB) showed that PHB from organic waste otherwise destined for landfill produced about half the energy and greenhouse gas emissions as PHB from a dedicated agricultural feedstock such as corn [100].

As discussed in this report, while some thermoset polymers can be up to 100% bio-based, resins are available or under development with very variable proportions and sources of bio-based content. It can therefore be seen that careful consideration needs to be given to the LCA analysis of these materials as they vary widely.

7.1.3 INTERDEPENDENCY OF FIBRE, MATRIX AND PROCESS

There are several software packages available to enable detailed LCA studies to be carried out. The Green Guide to Composites [101] illustrates environmental ratings for materials produced from natural and synthetic fibres combined with synthetic resins. The impacts of the various material choices and stages of production are considered and demonstrate the complexity of LCA for composite materials:

MATERIAL CHOICES

The matrix is made up of a polymer and often other components such as catalyst, accelerator and filler. Polymers based on fossil fuels have considerable environmental impact associated with their raw materials extraction, processing, manufacture and disposal. Due to the high proportion of the matrix and its inherent environmental properties, in most cases it will be the greatest cause of environmental impact for the composite product. There is currently a reasonable amount of LCA data relating to thermoplastic resins but much less relating to thermoset resins. However, LCA-based data is emerging to support the view of reduced environmental impact from part-bio thermoset resins [102.]

Glass fibre is used in a number of different forms, including rovings, woven fabrics, chopped strand mat and chopped fibres. Environmental differences occur mainly due to the differing energy requirements between the methods of producing the different fibre forms.

Carbon fibre has a relatively high environmental impact, closely linked to energy demand during its manufacture. However, for the same structural performance less carbon fibre is needed in a composite product when compared with other fibre types, so its comparative environmental impact is reduced.

Generally speaking, for natural fibres, whilst there are some impacts that arise from its cultivation, the energy demand is very low which results in a relatively low environmental impact.

However, when each fibre is combined with polyester resin, the impacts are changed. Although hemp performs best by weight, woven glass actually performs better in a panel with equivalent properties as it requires less material. Woven carbon, having even higher structural qualities, requires the least amount of matrix but still has the highest impact. The choice of process, and hence volume fraction, can also have an impact on the final assessment.

PROCESS CHOICES

Each stage of the manufacturing process has an environmental impact that contributes to the total impact for that FRP product, and there may be a number of choices for each manufacturing stage. These impacts of each manufacturing stage vary in their magnitude and range, and to select the best environmental option it is necessary to see which parts of the process contribute the most to the overall total. The embodied impacts of the materials have the largest environmental impact. However, depending on the process, many of the other stages can contribute a sizeable proportion of the total environmental impact. Not all of the choices within process stages are mutually exclusive and the choice of one may affect the magnitude and range of impacts of another.

This co-dependency is most evident within the choice of process, fibre and matrix. For instance, if a fibre of low environmental impact is chosen, it may not then be possible to choose the matrix with the lowest environmental impact. These choices also determine the amount of material needed for manufacture, where material quantity has a significant influence on the overall impact.

Research by a UK consortium, under a Defra funded project called BioCompass, collected data for bio-based fibres and resins and has produced an interactive web-based assessment tool, www.bre.co.uk/biocompass [103]. This website also includes relevant supporting information about materials and standards.

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BIOCOMPOSITES

7.2 DURABILITY

Biodegradable composite products from natural fibres and resins have certain useful applications that offer significant environmental benefits over other materials. However, for industrial applications long-term in-service durability is a key property and as yet is not fully understood.

There is much ongoing research on the durability of natural fibre composites both using synthetic and naturally derived polymer matrices. Key concerns centre around moisture ingress causing possible rotting of the fibres. Fibre treatments to reduce moisture uptake have been discussed in section 2.5. Recent research [39] has looked at the environmental degradation behaviour of flax fibres and their polymer composites. Duralin flax fibres, which have been treated by a novel process for improved moisture and rot sensitivity were studied. Environmental studies showed that these upgraded Duralin flax fibres absorb less moisture than untreated green flax fibres, whereas the mechanical properties of the treated fibres were retained, if not improved. Other research work has investigated the use of water glass, acetylation, dimethyl-dihydroxy-ethyelene-urea (DMDHEU) and silanization to treat fibres to improve durability although none have yet resulted in step-change in moisture uptake resistance [29].

A study at University of Southampton [104] compared the effect of hygrothermal ageing on the flexural properties of glass reinforced composites using typical epoxy resin and resins based on linseed oil and castor oil. For all composites a significant drop in mechanical properties is observed after a few days of accelerated ageing, and water ingress causes dramatic changes in failure modes. However, the castor-based resin was much less affected than the epoxy whereas the linseed-based resin was worst affected.

7.3 END-OF-LIFE OPTIONS

One of the key selling points of natural materials is their environmentally positive end of life options, which may include recycling, biodegradation or composting.

Some composite products are engineered to be biodegradable at the end of their service life. Natural fibres and some bio-based polymers can be degraded by micro-organisms and composted. In this way the CO_2 fixed by the fibre will be released and the cycle will be closed.

For non-biodegradable materials other end-of-life options are available, although the current most economic option is still landfill. Composite materials can be recycled, reused in some instances or burnt for energy recovery. The end-of-life 'disposal' route has a significant impact on the overall environmental rating for a product. Thermoplastic composites with glass fibre reinforcements can generally be granulated and reprocessed by injection moulding into lower grade products. However, recycling of natural fibre thermoplastics in this way may not be a viable route as natural fibres are degraded by repeated heating and processing steps.

It should also be noted that whilst recycling by grinding/shredding is technically possible for thermoset composites, volumes available currently do not make this an economic option, and there are few end-markets for the recyclate produced.

Energy recovery through incineration could be a desirable option. The benefit for incineration depends very much on the type and amount of combustible material in the final product. The reported net benefit for the incineration of polypropylene is 21.5 MJ per kg, whilst for a natural fibre the net benefit is 8.3 MJ per kg [96]. Since natural fibres (and bio polymers) do not use petrochemical sources they do not release additional CO_2 into the environment when incinerated.

7.4 SUSTAINABILITY

Durability, compatibility, affordability and sustainability are the challenges for converting renewable resources into industrial materials. Sustainable development provides growth of both ecological integrity and social equity to meet basic human needs through viable economic development over time. When a new material is designed and manufactured, one consideration should be sustainability, including resource availability, land use, biodiversity, environmental impact, energy efficiency, soil conservation, and the impact on the social community. Besides a favourable life cycle analysis, research and development of bio-based products should consider the limits that will maintain sustainable development. The design of bio-based materials should favour increased materials supplements, optimised land use, improved bio diversity, minimised environmental pollution, and improved energy efficiency, while at the same time meeting consumer demands.

Large proportions of biomass are available each year for energy use – these include energy crops, biogas, crop residues and other wastes. Some of these residues will be returned to the land to maintain soil quality and some are used for animal bedding or manure, but around 70% of these crops may be available for energy use [58].

Where waste product utilisation for the production of natural fibres and resins has clear advantages, social environmental issues become increasingly important where non-food crops are grown in preference to food crops. Non-food crop production is limited by land availability. Fibre crops grown with an end-use contract in place are eligible to be grown on set-aside land in the UK. A Home Office licence is required for the cultivation of industrial hemp. However, farmers can now grow hemp under a license obtained by their processor. There is an opportunity to increase production of fibre crops in the UK. In particular, opportunities lie in establishing regional processing and manufacturing facilities. The transport of bulky raw materials across large distances brings increased costs and diminishes environmental benefits.

It is clear that the analysis of the impacts of the materials and processes that might be used for biocomposites is very complex. One way to navigate through the complexity might be to use a Quickscan methodology, developed in the BioBuild [105] project, which uses LCA principles to (relatively) quickly decide on which option available has the least environmental impact.

8 CURRENT AND FUTURE APPLICATIONS

Natural composites have a vast range of potential applications, from small consumable components to large semi-structural parts. A significant number of commercial applications exist and these are increasing rapidly as companies look to switch to more sustainable materials. The usage levels of different natural materials reflects their respective stage of development. For example, natural fibre-reinforced petrochemical polymer composites are already in widespread use, whereas natural fibre-bio-based polymer composites have only recently been applied commercially. The main current markets for biocomposites are automotive, construction, sports/leisure and consumer goods.

8.1 AUTOMOTIVE

In the automotive sector, the main natural composites used are wood plastic composites (WPCs), short natural fibre injection moulding compounds and non-woven natural fibre mats. However, woven continuous natural fibre mats are also starting to become a viable option for more demanding applications, extending the range of potential applications. Petrochemical polymers are most-often used at present, although bio-based polymer composite parts are emerging. Typical automotive applications include trim parts, dashboard parts, door liners, parcel shelves, and load floors.

In 2012 the European automotive industry used 90,000 tonnes of natural fibre composites and 60,000 tonnes of wood plastic composites [106]. Of the 150,000 tonnes total, wood was the main fibre used, followed by recycled cotton (25%) and then flax (19%). Kenaf accounted for 8%, hemp 5% and the others (jute, coir, sisal, abaca etc.) made up 7%. On average, every new car produced in Europe contains around 4 kg natural fibres in composite materials, rising to 25-30 kg in some cases.

Commercial applications of natural fibre-bio-based polymer composites have been relatively limited to date. Toyota have developed automotive parts from press moulded kenaf-PLA non-woven mats, including the Toyota Raum spare wheel cover, which is claimed to be the first 100% natural automotive product in the world [85] (although Henry Ford was experimenting with hemp-reinforced soy resin panels for cars as early as the 1940s). Soybean-natural fibre composites have been used commercially by John Deere, under the trade name HarvestForm®, to produce body panels and cab roofs for hay balers. The parts were produced by the RIM process and 25% weight savings are claimed. More recently, EcoTechnilin (UK) has supplied a composite sandwich panel consisting of non-woven flax / bioresin facings and a paper honeycomb core (“Fibricard”) for a load floor in the Jaguar F-type convertible (Figure 14).

Figure 16: Flax / bioresin / paper honeycomb sandwich by EcoTechnilin. Photo:Stella Job, Materials KTN

8.2
CONSTRUCTION

In construction, WPCs are used in significant quantities. In fact, WPCs are probably the largest market for natural fibre composites at present. In 2012, approximately 260,000 tonnes of WPC were produced in Europe with about 175,000 tonnes being used for decking. Demand is expected to increase. North America is a much larger market; 1.1 million tonnes were produced in 2012. China (at 900,000 tonnes) is set to overtake North America. The most important applications for WPCs are decking, railings, outdoor furniture, picnic tables, garden benches, pallets, boards, etc.

In June 2009, a pavilion made with a range of sustainable materials and technologies, including biocomposites, was opened at the Louisiana Museum of Modern Art, Denmark. This interactive sculpture, designed by the architecture firm 3XN, is made from a range of eco-friendly technologies including natural fibres and bio-based polymers, solar cells and self-cleaning coatings.

Figure 17: Pavilion at the Louisiana Museum of Modern Art, Denmark, made from sustainable materials including biocomposites (photo used with kind permission of 3XN, Denmark).

In 2013 a full biocomposite building façade was installed in the Netherlands. This gas receiving station is clad with bio-based panels made from hemp fibre and a bio-based resin. Each of the 104 panels is 140x185 cm and made from 'Nabasco' (Natural Based Composites).

Figure 18: A bio-based façade made from hemp and part-bio resin (Gas receiving station clad in biocomposite panels. Location: Agro and Food Cluster, New Prinsenland, Netherlands. Architect: Marco Vermeulen. Manufacture: NPSP Composites, Haarlem. Photo ©Robert Tilleman).

As mentioned previously, the manufacture of biocomposite panels is entirely feasible, the challenge in the construction sector is to achieve durability for external use (moisture, microbial attack and UV resistance).

Outside of the fibre-reinforced composites sector, natural fibres are used as insulation materials, thatch roofing and geotextiles. One interesting application of hemp shive, a waste product of hemp fibre production, is hemp-lime which can be used as blocks or sprayed onto walls to provide structure and excellent insulation properties. For example, Hemcrete hemp-lime was used in the construction of the Adnams Brewery warehouse in Suffolk, UK, where it enables the building to remain at a constant 16 ^{o}C without the use of heating or air conditioning, saving approximately £40,000/year in energy costs [86].

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8.3
SPORTS AND LEISURE

There are many examples of where biocomposites have been used successfully in sports and leisure applications, particularly for outdoor sports where there is a clear marketing synergy with natural materials. Snowboards (Figure 17), canoes (Figure 18), surfboards and bike frames have all been produced using woven flax reinforcements materials. The excellent vibration damping properties of flax have also seen it used in conjunction with carbon fibres for high performance sporting goods that are prone to impact, such as ice hockey equipment.

Figure 19: Snowboard by Magine, manufactured from Composite Evolution's Biotex flax fabric.

Figure 20: Canoe, by Flaxland, manufactured from Composite Evolution's Biotex flax fabric.

8.4
CONSUMER PRODUCTS

Figure 21: Biocomposite furniture developed by NetComposites and Sheffield Hallam University, Design © Roger Bateman Sheffield Hallam University.

Within the area of consumer goods, WPCs and short natural fibre compounds are of most interest, as they can be injection moulded into complex shapes in high volumes. Bio-based polymers are also likely to be adopted more readily in this market due to the demand from environmentally-minded customers coupled with the possibility of lower mechanical performance requirements. Potential applications include furniture, tableware, handles, electrical goods, rigid packaging, plant pots and mobile phones.

An interesting piece of bio-based furniture has been developed by a partnership of NetComposites and Sheffield Hallam University Art and Design Research Centre using a combination of moulded biocomposite panels and wooden structure (Figure 19). The panels are made from Biotex (supplied by Composites Evolution Ltd), a flax plus polypropylene (PP) or Polylactic Acid (PLA) textile which is thermoformed into shape from a woven textile. The panels can be arranged in a modular fashion to create many varieties of furniture.

Another successful application has been the manufacture of boxes and covers for outdoor grit storage, developed as part of the NATEX FP7 project [25], shown in Figure 20. This uses two types of aligned flax reinforcements in the lay-up - Biotex Flax +/-45 biaxial non-crimp fabric (600 g/m^2) and Biotex Flax 4x4 hopsack woven fabric (510 g/m^2). The grit box cover also contains polyester resin and flax fibres manufactured through a cold pressing technique.

Figure 22: Grit Box manufactured by CEMO GmbH.

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9 CONCLUSIONS

A wide range of natural fibres can be used for composite reinforcement but flax, jute and hemp are the most commonly used as they have the highest mechanical properties. Fibre quality is significantly influenced by the retting and fibre extraction methods used and currently there is a move towards mechanical processing (decortication) of 'green' (unretted) fibre to improve consistency and reduce costs. For composite reinforcement, the fibre length must be preserved and the impurity (shive) content must be low. Aligned natural fibre yarns and fabrics offer higher mechanical properties than short, random fibre reinforcements but the yarns must have low twist so that the fibres remain on-axis and they can be fully impregnated by resin. A range of treatments have been investigated to reduce the hydrophilic characteristic of natural fibres and improve compatibility with polymers and, of these, acetylation currently appears to be of most interest.

A number of bio-based polymers are commercially available and many more are under development. Thermoplastic bio-based polymers based on starch and polyesters, such as PLA (e.g. Natureworks®) and PHB, are used widely in packaging applications. They are currently more expensive than synthetic commodity polymers and often require plasticising or impact modification due to their brittle nature. Thermosetting bioresins from soybean, linseed oil or polyfurfuryl alcohol (PFA) are currently used less widely but have good potential in the composites industry. In the short term, blended resins containing both bio and synthetic constituents such as bio-based unsaturated polyester resins, bio-based epoxies (using soybean oil or cashew nut shell liquid) and polyamides based on castor oil, offer good performance with lower environmental impact.

Composites based on natural fibres and synthetic polymers are now used in significant quantities in industry. Wood plastic composites (WPC), consisting of very short wood fibres and PP, PE or PVC, are used to make decking, railings, outdoor furniture and automotive parts. Compatibilisers are often used to improve fibre-matrix bonding, such as maleic anhydride for PP. Short natural fibre-PP pellets are generally compounded using twin screw extruders and then injection moulded into automotive parts and consumer goods. Non-woven natural fibre mats, usually containing PP or PU binders, are press-moulded in large quantities to make automotive door liners, parcel shelves, trim etc. and have also been used in the resin transfer moulding process, where pre-drying of the natural fibres is important. Aligned natural fibre fabrics are starting to be used to obtain higher mechanical performance, for example to make woven flax-epoxy prepregs.

Fully bio-based composites, containing natural fibres and bio-based matrices, have been under development for several years and some are now being used commercially, most notably short wood fibre-lignin and short flax fibre-PLA. Non-woven natural fibre mats are available with PLA or PFA binders and Toyota make some automotive interior parts from kenaf-PLA mats. In the US, natural fibre-soybean resin composites have been developed. Aligned natural fibre biocomposites have received less attention to date but, recently, an aligned flax-polyfurfuryl alcohol prepreg has been developed.

Regarding life cycle assessment, natural fibres are generally considered to have lower environmental impact than glass fibres due to reduced CO_2 emissions and energy consumption during production. During the use phase, natural fibres can have a significant positive impact on the environment, for example through reduced weight, energy consumption and emissions in the automotive sector. A recent environmental study on composites identified that resins have higher environmental impacts than fibres, so the development of bio-based polymers is particularly important. The durability of natural fibres, particularly their resistance to moisture, requires more investigation. A number of treatments have been developed to reduce moisture uptake and resistance to fungal attack. At the end of life, natural fibre composites can be recycled (especially if used with thermoplastic polymers), biodegraded (when used with biodegradable polymers such as PLA), or can be incinerated for energy recovery (unlike glass fibres).

A range of applications exist for natural composites, from small components for consumer and leisure markets to large semi-structural parts in the automotive and construction industries. Commercial applications of natural fibre-synthetic polymer composites include WPC decking and outdoor furniture and automotive parts such as door liners, parcel shelves and trim panels. Technology demonstrators such as the gas receiving station façade by NPSP have shown that natural fibres can be used successfully in conventional composites processes. To date, applications of fully bio-based composites have mainly been limited to niche products and concept projects. However, the demand from designers, manufacturers and consumers for environmentally friendly products will inevitably drive the rapid development of new biocomposite materials and products. In particular, the development of aligned, natural fibre fabrics suitable for composite reinforcement will provide significantly enhanced properties and will open the door to a range of semi-structural applications. In the medium term, improvements in the processing characteristics and properties of thermoplastic and thermoset bio-based polymers will facilitate the production of 100% natural, engineering composite materials.

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11 GLOSSARY

A

Acetylation: a treatment for natural fibres which uses acetic acid and reduces moisture sensitivity

B

Bast: a type of natural fibre present in the stem of many plants

Bio-based / bio-derived: made from natural, renewable raw materials

Biodegradable: material which can be broken down by microorganisms

Biocomposite: composite material where at least one of the constituents is derived from biomass origin

Bio-based polymer: polymer in which constitutional units are totally or in part from biomass origin. Bio-based polymers are not identical to bio-polymers. Bio-based polymers can be made synthetically from monomers derived from biomass, while bio-polymers are made directly by the living organisms

Bioresin: resin, typically thermosetting, derived fully or partially from natural, renewable raw materials

C

Carding: a process used to disentangle fibres, most commonly achieved using machinery with rotating drums covered with pointed wire, pins or teeth

Cellulose: glucose-based polysaccharide present in the cell walls of plants which can be used to produce polymeric or fibrous materials

Compostable: material which biodegrades in controlled conditions to yield CO2, water, inorganic compounds and biomass at a rate consistent with other known compostable materials and leave no visible, distinguishable or toxic residue and results in a compost-like material which supports plant life and does not contain toxins (see international standards, such as ASTM D6400-12 and BS EN 13432)

Coupling agent: an additive or surface treatment used to promote fibre-matrix adhesion

D

Decortication: mechanical process for extracting bast fibres from the stem/straw e.g. hemp

Degradable: material which breaks down into smaller molecules or fragments through chemical reactions

Dew retting: retting process whereby the straw is pulled and left lying on the field to decompose naturally in the presence of moisture

Duralin: fibre treatment based on hydrothermolysis which improves the moisture resistance and thermal resistance of flax fibres

Duvex: cylindrical rotating drum/sieve which removes the very short fibres and dust from longer fibres

E

Enzymes: complex molecules of protein produced by living cells, which act as catalysts in bio-chemical reactions and can be used in retting

F

Flax: plant containing natural fibres suitable for composite reinforcement (linen is made from its fibres and linseed oil comes from its seed)

H

Hackling: the process of combing flax fibres in order to remove short fibres and debris and align the long fibres

Hectare: 10,000m2 or 2.5 acres

Hemi-cellulose: similar to cellulose but composed of pentose sugars or hexose sugars other than glucose

Hemp: plant containing natural fibres suitable for composite reinforcement

Hurd: non-fibrous woody particles produced as a by-product of scutching

Hydrophilic: water loving, e.g. natural fibres

Hydrophobic: water hating e.g. synthetic polymers

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J

Jute: plant containing natural fibres suitable for composite reinforcement, widely cultivated in south and east Asia

L

Life Cycle Assessment (LCA) or Life Cycle Analysis: process of quantifying the environmental impact of a process or product, taking into account social, environmental and economic factors

Lignin: natural matrix material which binds the strong and stiff cellulose units together in, for example, natural wood

N

Non-woven mat: mat product consisting of relatively short, randomly oriented fibres, usually needle punched to provide mechanical binding

P

Pectin: structural polysaccharide found in the cell walls of plants

Polyfurfuryl alcohol (PFA): A thermosetting resin based on furfuryl alcohol derived from agricultural wastes

Polyhydroxyalkanoates (PHA): family of bio-based polyesters which are produced through fermentation by microorganisms fed with glucose

Polyhydroxybutyrate (PHB): bio-based polyester from the PHA family

Polylactic acid (PLA): bio-based polyester which is made most commonly from corn starch

Polysaccharides: large class of natural carbohydrates including cellulose and starch

Pulling: the process of pulling flax plants out of the soil during harvesting rather than cutting them as is usual with other crops

R

Regenerated cellulosic fibres: fibres made by dissolving cellulose in a solvent and then spinning from the solution, e.g. viscose and rayon

Retting: the decomposition of crop stems by biological or chemical processes to enable the fibres to be separated more easily, e.g. dew retting, enzyme retting, water retting

S

Scutching: the process of removing fibres from broken straw to remove shive and other debris. Most commonly used for flax

Shive or Shiv: woody matter of flax stalks removed during scutching

Sliver: a loose, aligned tow or bundle of fibres, often used as a precursor to yarn spinning

Spinning: the process of drafting and twisting of fibres into a yarn

T

Tow: an assembly of a number of fibres or filaments in a loose strand, usually without twist

Turning: the process of manipulating the flax straw lying on the field to ensure uniform retting

W

Water retting: process of retting by immersion in pools of water (now mostly superseded by more environmentally friendly techniques)

Weaving: process of producing a textile fabric by interlacing yarns

Wood Plastic Composites (WPC): composite material consisting of short wood fibres/flour in a thermoplastic polymer matrix, most commonly PP, PE and PVC

Y

Yarn: a continuous product composed of fibres or filaments, with or without twist

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