Functionality and Properties of Bio-based Materials

Pintu Pandit, Gayatri T. Nadathur, Saptarshi Maiti, and Baburaj Regubalan

Abstract This chapter reviews the impact of recent developments in bio-based sustainable materials with enhanced functionality and its properties related to moisture permeability, porosity and tunable gas permeability characteristics on storing and packing wet and dry foods and fresh produce. Bio-based polymers, plastics, biodegradable plastics and composites are gaining interest as reasonable substitutes for non-renewable petrochemical-based products. Natural fibres such as jute, hemp, flax, banana, wheat straw, etc. are significant sources for making biodegradable composites having commercial importance as food packaging materials. Combining plant-based fibrous materials and biopolymers/biomass-derived polymers gives environmentally friendly and biodegradable biocomposites with sufficient flexibility and mechanical strength comparable to petroleum-based polymers. Improved mechanical resistance, thermal insulation and enhanced physico-chemical properties which are key to the barrier and permeability features in bio-based packaging materials are achieved. Protein-based materials, which demonstrate good barrier properties, being impermeable to oxygen (in the absence of moisture) and aromatic compounds, have also been investigated as potential food packaging materials. This chapter presents a review of the literature available on such processes, techniques and methods applied to exploit these sustainable bio-based materials.

Keywords Bio-based polymers · Biodegradable · Physico-chemical properties · Food packaging

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P. Pandit (✉) · G. T. Nadathur · S. Maiti
Department of Fibres and Textile Processing Technology, Institute of Chemical Technology, University Under Section -3 of UGC Act, Mumbai, India

B. Regubalan
Department of Food Engineering and Technology, Institute of Chemical Technology, University Under Section -3 of UGC Act, Mumbai, India

S. Ahmed (ed.), *Bio-based Materials for Food Packaging*,
https://doi.org/10.1007/978-981-13-1909-9_4

1 Introduction

A green and sustainable economy requires that a revolution occurs in the utilization of raw materials; it needs to substitute the overwhelming consumption of fossil fuel-based materials with processes and products obtained from plant-based and other renewable resources. Solar and wind power could likely drive the change in the energy supply sector, while the change will be driven, within the manufacturing industry, by bio-based materials and their composites in different applications such as food packaging, textile fibrous materials, geotextile, plastics industry, etc. (Storz and Vorlop 2013).

Bio-based materials have gained attractiveness in the last decades due to both ecological and economic concerns. The increased burden of pollution and waste has motivated the scientific and industrial communities to look at bio-based substitutes for fossil fuel-based materials. Bio-based materials can be synthesized mainly by the production of polymers directly from naturally occurring compounds or the production of bio-based monomers and their subsequent (bio)chemical polymerization, through processes such as fermentation. Whatever the pathway for production of bio-based materials, the main problem is to control its composition and reproducibility. The regulation of the size of the biopolymers appears even more complicated. In any case, the major hurdle is in making the (micro) organism perform the targeted biosynthesis consistently and repeatedly. To overcome this problem, one can be tempted to make more controlled chemical polymerization with the bio-based monomers. However, the polymerization of bio-based monomers often demands further developmental steps, as in the case of a polylactic acid and of polybutylene succinate. The production of partially bio-based materials (Soronas) or the production of bio-monomers identical or enhanced compared to currently used petroleum-based molecular units has been demonstrated (Storz and Vorlop 2013; Razzaq et al. 2016).

A simple method for the simultaneous extraction of protein and β-glucan and polymers from barley was employed to prepare biodegradable films. Cereal grains are sustainable sources of polymers that could be used to make environmentally friendly bio-based materials. The procedure was customized in that the extraction was completed in alkaline medium instead of normal pH water. Likewise, the good macroscopic performances of the film and the assessed chemical stability could suggest its first-line applications as a newer, cheaper and biodegradable plastic material for food packaging (Razzaq et al. 2016). A lot of research has taken place on the methods to convert these sustainable options into films, fibres, textiles, papers, packaging or any other form which has a prospective application in the field of bio-based materials.

With the increased importance placed on self-service marketing, the role of bio-based packaging materials is becoming quite significant. Bio-based packaging materials serve numerous purposes like physical coverage, information transmission, marketing, convenience, barrier protection and security. Currently, several bio-based materials like polymers, paper (brick carton, cardboard), foam, film, etc. exist as options to synthetic plastic which is the most common packaging material but problematic and costly with respect to disposal. The features common with all plastics are that they are light, strong, cheap to manufacture and easy to mould. Paper gets preference in food and textile packaging. The cardboard variety of paper used in the form of boxes, sheets, etc. has served as a container for pizzas, bread and pies, popcorn, coffee, chocolates and other takeout order from the fast-food restaurants (Johanson and Vahlne 1977; Sullins et al. 2017; Yan et al. 2014). This chapter presents a critical review of the current literature available on such processes and techniques that modify the functionality and characteristics of bio-based materials to exploit and utilize them to their fullest.

2 Classification and Methods of Bio-based Materials

2.1 Classification of Bio-based Materials

Bioplastics are not simply a uniform single class of polymers but a diverse class of materials that can differ significantly from one another. The term bioplastics denotes materials that are bio-based, biodegradable or both (refer Fig. 1).

The use of bio-based materials, i.e. fibres, paper, plastic coatings and solid articles made from sugar, corn, starch and other renewable raw materials, has multiplied in recent times. Biopolymers find versatile applications in drug delivery systems, surgical implant devices, scaffolds for tissue engineering and packaging, food containers, agriculture film, waste bags and packaging material. Biopolymers often have a firm and definite internal structure, though this may not be the main feature (e.g. lignocellulose).

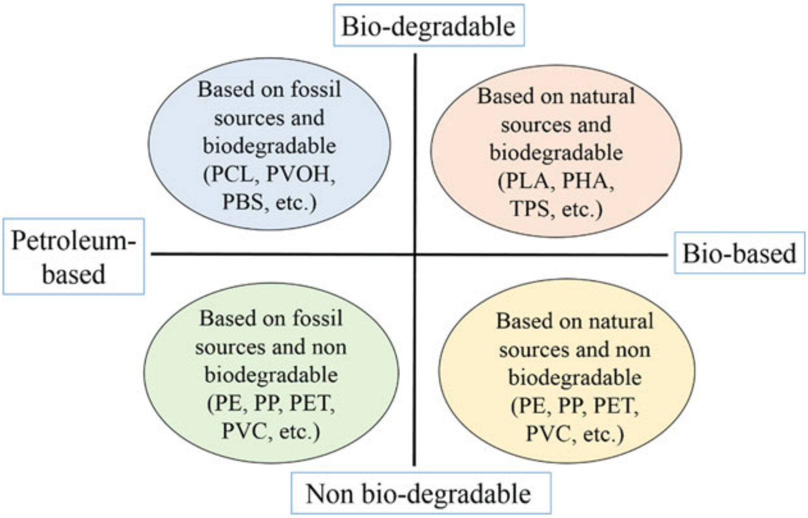

Fig. 1 Classification of bioplastics based on source and degradability

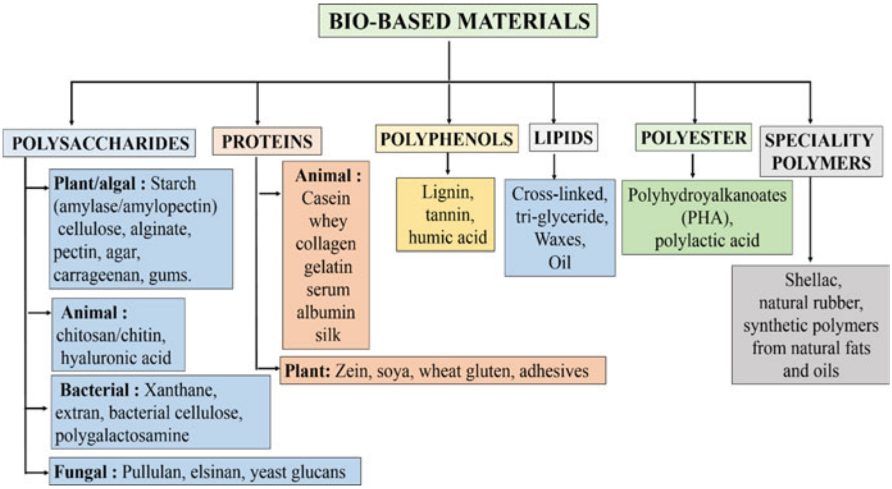

Fig. 2 Classification of bio-based materials

Among the biopolymers, polyethylene furanoate is observed to possess better mechanical properties. Cross-linking agents (e.g. glutaraldehyde, polycarboxylic acids) enhance the mechanical properties and aqueous stability of the biomaterials but may cause unfavourable modification to the functionality of the biopolymers or cause cytotoxicity (Türe et al. 2012; Petersen et al. 1999). All kinds of natural fibres like flax, bamboo and natural wool can be bonded together with synthetic and bio-based adhesives to form useful fibre-reinforced biocomposite composites (refer Fig. 2).

2.2 *Methods for Manufacture of Bio-based Materials*

Overall, there are three pathways to produce biopolymers as per the literature (Petersen et al. 1999; Weber et al. 2002).

(a) Directly extracted or separated from biomass
(b) Generated by microorganisms (fermentation) or genetically modified bacteria
(c) Manufactured by classical chemical synthesis from biomaterials

The basic repeating chemical units of the bio-based materials are almost similar to those of conventional plastics. The main processing route of bio-based materials can also be possible by this method of technology:

(a) Packaging film: extruded film, blown films, cast film
(b) Thermoformed sheets: trays, cups
(c) Injection moulding: drinking beakers, bottles, trays cutely, cups, plates, etc.

(d) Fibres and non-woven: diapers, feminine hygiene products, agricultural products, certain medical plastics, clothing
(e) Extrusion coating: laminated paper or films

3 Properties of Bio-based Materials

General attributes for enhanced properties and functionality of bio-based materials must be efficient, effective, clean and recyclable. The bio-based materials provide tremendous encouragement to green manufacturing by successfully enclosing and shielding products which are key properties for packaging. Also, the packaging system is intended to use materials and energy with minimal waste throughout the product life cycle. The properties that need to be reckoned with respect to food bio-based materials may include gas and water vapour permeability, sealing capability, thermoforming properties, transparency, antifogging capacity, printability, availability, UV resistance, water resistance, and resistance to acid, alkali, grease, etc. Cost is also one of the important properties for bio-based materials. Thus, bio-based materials in relation to end applications in food and other industries require favourable mechanical, thermal and gas barrier, water vapour permeability features and disposability of the materials. A product that contains 100% annually renewable raw materials may or may not be biodegradable/compostable. It is conditional on the molecular structure of the material itself, and if biodegradable, the products would pass when tested for biodegradability and compostability according to ASTM D6400 or ASTM D6868.

3.1 Gas Barrier, Moisture Resistance and Water Vapour Transmittance Properties

Many bio-based food packaging materials need the presence of specific atmospheric conditions to maintain the freshness and quality of food during storage. The packaging materials need to have certain gas barriers to retain a constant gas composition within the package. The gas mixture inside most of the package contains carbon dioxide, oxygen and nitrogen. Bio-based materials by using mineral oil-based polymer provide gas barrier property. Gas barrier properties of PA6 (polyamide) or EVOH (ethylene vinyl alcohol) which are vulnerable to moisture, when combined with LDPE, create a very restrictive water vapour barrier preventing the moisture from the foodstuffs interfering with the properties of PA6 or EVOH. Plasma technology was used for the deposition of glass like SiOx coatings on bio-based materials out of natural polymer and modified clay to enhance water vapour and gas properties (Fischer et al. 2000). Bio-based materials are mostly hydrophilic, and the gas barrier properties are influenced by the humidity conditions, such that the gas permeability of hydrophobic bio-based materials may increase drastically when humidity increases. Gas barriers based on PLA and PHA are likely to be independent of humidity (Petersen and Nielsen 2000).

Packaging for numerous food types requires materials that are impervious to moisture, which is a major challenge due to the contrary hydrophilic nature of most of the bio-based polymers. Inventive chemical modifications and treatments are being researched to solve this problem so that future bio-based materials must also be able to duplicate the water vapour barriers of the conventional materials. In many of the bio-based food packaging applications, water vapour barrier, along with gas barrier properties, is required.

3.2 Physical Blending and Chemical Processing

Current research in the properties of bio-based composite materials involves the development of technologies to innovate chemical and physical modifications for optimal composite properties related to air, water permeability, water resistance/hydrophobicity, surface properties of adhesion and frictional resistance, mechanical strength, fracture resistance, fire retardance, sound barrier, thermal insulation and optical and conductive properties.

Composites of bio-based materials find their major use as structural components in textiles, packaging and disposables, which may be extended to greater strength bearing the use in construction and transportation sectors, for obtaining weight reduction to aid fuel efficiency and reduce cost, without compromising on load-bearing ability. This may be achieved if properties, processing and hence performance are improved by suitable chemical and physical modifications. In the addition of bio-based reinforcing fibres in composites, this implies control of reinforcement orientation/alignment and concentration, the addition of nanofibres and nanoparticles to optimize mechanical, thermal features and increase durability.

3.3 Improvement in Mechanical Properties

Most of the bio-based materials function in a similar manner to conventional polymers. Bio-based polymers similar to polystyrene-like polymers relatively stiff at moderate service temperature or polyethylene-like polymers relatively flexible at moderate service temperature are available. The mechanical properties in terms of modulus and stiffness are quite close to those of conventional polymers. Bacterial cellulose polymer could be used in materials requiring noteworthy mechanical properties (Iguchi et al. 2000).

In terms of use of plant fibre/lignocellulosic fibre-reinforced composites/plastics as engineering materials, the important structural properties of tensile strength relative to the density of the material lie in the upper left region of the Ashby's

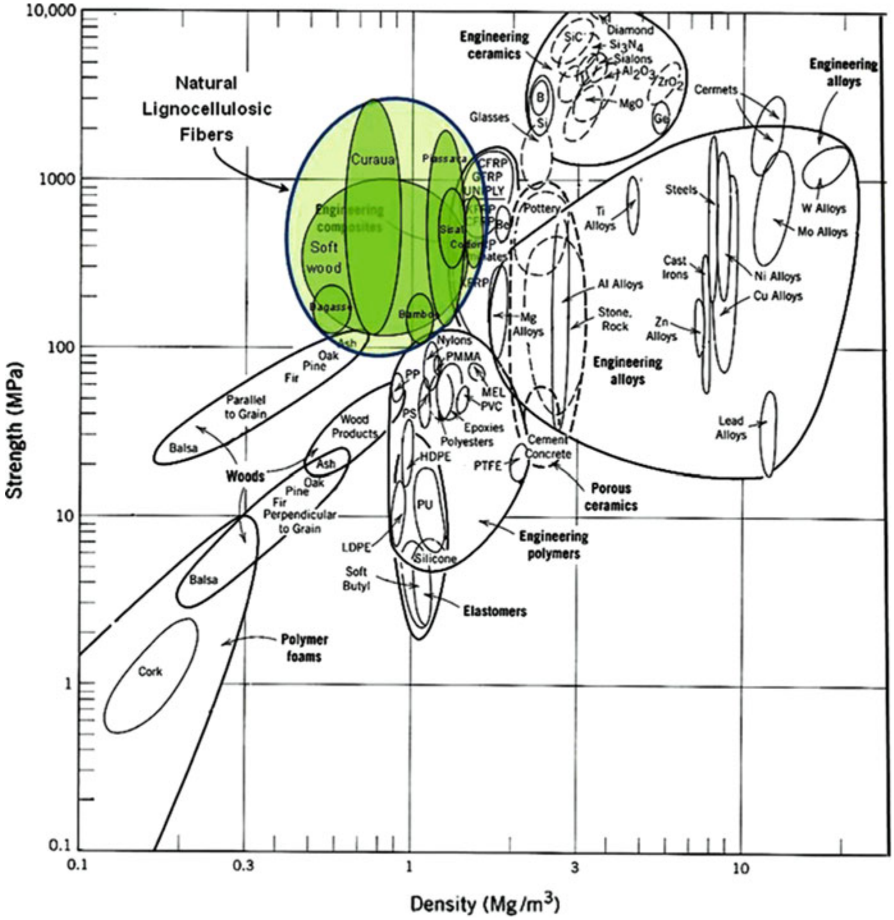

Fig. 3 Lignocellulosic fibres in Ashby's σ vs. ρ chart. (Monteiro et al. 2011)

material property chart (Fig. 3) (Monteiro et al. 2011). Their highest strength values are comparable to metallic alloys and ceramics and are favourable choices suiting guidelines of minimum weight design ($\sigma^{2/3}/\rho$, indexing the performance of a material related to bending stresses) and efficient mode of loading ($\sigma^{1/2}/\rho$). The existence of structural defects and dimensional heterogeneity in the natural source of plant fibres are a disadvantage that may be overcome by genetic selection and bioprocessing, for final use as high-performance thin fibres in composites. It was observed that plant fibres function as superlative reinforcement for polymers when the orientation of the fibres is unidirectional to the loading direction and the fibres are long. Tensile moduli and strengths of up to 40 GPa and 450 MPa, respectively, were reported for unidirectional plant fibre composites containing between 40 and 60 weight % flax, hemp, jute or ramie fibres (Fortea-Verdejo et al. 2017).

The tensile strength of glass fibres is at least twice as high as the tensile strength of plant fibres. Glass fibres are however inherently heavier than plant fibres (the density of glass fibres is 2.5 g cm^{-3} versus ca. 1.5 g cm^{-3} for plant fibres). Despite this, some randomly oriented plant fibre-reinforced polymer composites have very similar mechanical properties compared to randomly oriented GFRP, especially at low w_f (fibre loading fraction). At $w_f > 50$ wt-%, the tensile strengths of plant fibre-reinforced polymers showed lower values for tensile modulus and strength compared to PLLA (the bio-based polymer with the best mechanical properties). This may be due to the random orientation of plant fibres within the polymers, causing greater plasticity and hence lower tensile properties of the resulting composites. This situation is exacerbated when very short fibres are used, which may also be generated during the processing, resulting in less effective stress transfer from the matrix to the fibres. Constructive fibre reinforcement is achieved when the length of the fibre exceeds the critical fibre length (which is affected by the fibre-matrix combination and method of manufacturing), the fibre tensile strength at the critical length and the fibre diameter. Plant fibres substitute as cheaper filler possessing competitive stiffness, strength and fatigue properties compared to conventional engineering (polymer, glass or carbon) fibres, replacing some portion of the costlier polymers, leading to reduced costs while increasing the renewable fraction of the end composites.

The fabrication of bio-based anisotropic hierarchical fibres, combining small amounts of functionalized recombinant spider silk proteins with the widely available structural constituent, cellulose nanofibrils (CNFs), resulted in, for the first time, highly desirable mechanical performance with a stiffness of ~55 GPa, strength at break of ~1015 MPa and toughness of ~55 M m^{-3} (Mittal et al. 2017). The addition of small amounts of silk fusion proteins to cellulose nanofibrils (CNF) produced materials with advanced functionalities, which cannot be derived from wood-based CNF alone. The silk/CNF fibre surfaces also exhibited bioactivity allowing chemical-free immobilization of antibodies and adhesion of fibroblasts promoting their growth and spread, compatible with tissue culture, ascribed solely to the proteinaceous component of the silk.

Poly (L-lactide) (PLLA), a bio-based polymer, based on L-lactic acid, exhibits high tensile strength and Young's modulus, while its impact strength and heat deformation temperature (T_d) are notably low. To improve upon the properties of PLLA, a stereocomplex-type PLA (sc-PLA), obtained in a mixture (50/50) of preformed PLLA and PDLA, was developed (Ikada et al. 1987). The improved thermal resistance of sc-PLA is the reason why sc-PLA-based woven and knitted clothes can be treated to dyeing and hot-pressing and a knit of sc-PLA withstands laundering above 160 °C. In contrast, PLLA fibres are heat-sensitive, and processing above 120 °C destroys the fibre structure (Fan et al. 2004). When polymer films made by solution casting were studied by Tsuji and Ikada, the mechanical strength of sc-PLA was observed to be almost 60% higher than that of PLLA (Tsuji and Ikada 1999). The melt spinning of an oriented fibre of sc-PLA gave a product with very specific tensile strength and Young's modulus of 400 MPa and 5 GPa, respectively, in comparison to ordinary melt-spun fibre of PLLA which exhibited a greater range in tensile properties (Takasaki et al. 2003; Fukushima and Kimura 2006). Polymer films of sc-PLA may be used as heat-resistant insulators that are also optically transparent. The incombustible nature of PLA, having an oxygen index of 28, could be used in casing material for various electrical devices and automobile parts.

A polymer blend between PLA and natural rubber, which is a totally bio-based polymer, modulates the brittleness of PLA (strain at break ~5%), with NR as a toughening agent, to obtain a modulus of 300%. Ordinarily, thermoplastic elastomers are prepared from ductile polymers like polyethylene and nylon, rather than brittle plastic like PLA. Bio-based thermoplastic elastomers (TPE) made of natural rubber and poly(lactic acid), with a blend ratio of 60% of natural rubber and 40% of poly(lactic acid), were prepared by melt blending in an internal mixer (Tanrattanakul and Bunkaew 2014). The addition of plasticizers, such as tributyl acetyl citrate (TBAC), tributyl citrate (TBC), glycerol triacetate (GTA) and triethyl-2-acetyl citrate (TEAC), would increase the ductility of PLA by increasing the strain at break, on interaction with the continuous phase of plastic PLA, the solubility parameter of plasticizers being similar to PLA rather than NR. All plasticizers, except GTA, increased the tensile toughness of the TPE as indicated by the area under each stress-strain curve.

Blends with PE and starch displayed lower elongation values, tensile strength and tear strength but also that the mechanical strength parameter was dependent on the amount of plasticizer compared to synthetic polymers, LDPE and HDPE. The compression tests done on the cup forms indicated favourable results. PLA has values (around 280 N) similar to those of PS (polystyrene), while starch composites gave high values greater than 1000 N. In terms of water vapour permeability, increased starch content increased WVP, while PLA and PHB and cellophane showed lower values, favourable to prevent loss of moisture from fresh produce (Petersen et al. 2001).

3.4 Thermal Insulation Property

Rigid polyurethane (PU) and polyisocyanurate (PIR) foam materials are largely used as heat-insulating materials in the refrigeration industry and civil engineering due to its low thermal conductivity (λ), and other PU compositions are applied in coatings and adhesives. Renewable materials in the form of polyol, a hydroxyl derivative of vegetable and other natural oils, were incorporated into the PU polymer matrix, through condensation with isocyanates to give the PU product. Polyol sources which do not coincide with food sources, such as rapeseed oil, and nonagricultural mixtures, such as those of abietic acid and oleic acid, a by-product of cellulose production may be used, after transesterification with polyfunctional amine-based alcohol, like triethanolamine. Thermal insulation products with competitive fire retardance substituting halogenated fire retardants with nanosized expanded graphite and IF, a commercial product, based on mineral and glass fibres with inclusion of graphite particles, and co-introducing isocyanurate structures into PU matrix were approaches used for sustainable solutions (Kirpluks et al. 2016). The thermal conductivity of 22.0 mW/m·K, considered in the industry to be a standard for thermal insulation materials, is in the range of vegetable polyol-derived PU/PIR. Expanded graphite and EG in combination with polyphosphate-based conventional fire retardants, however, increase in thermal conductivity from the industry required standards, in comparison with IF alone. Increased isocyanurate content to an index of 200 increased the mechanical strength unlike the swelling and plasticization of PU foam microstructure introduced by EG. The use of adhesives was not required in the coating of IF on PU sandwich panels, achieving thermal insulation with decreased flammability. On flame exposure, they did not ignite but formed protective char layer on the surface with reduced smoke production. Isocyanurate cross-linking also favours fire retardance. Thus bio-based polyols, in combination with nanoparticles, may be used to develop sustainable flame retardants, in polyurethane-based materials, while substituting for petroleum-derived chemicals.

3.5 Improvement in Air Insulation Constructions

The use of bio-based insulation materials has expanded recently, typically within breathable wall constructions, despite the need to compensate for their poor hygrothermal characteristic, (exposure to moisture and heat lowering their mechanical properties), by chemical treatments and blending with a synthetic polymer. An air-permeable wall construction enables the insulation material to influence the indoor air quality. Volatile organic compounds (VOCs) with low range boiling points between 60 and 280 °C contaminate indoor air in buildings, and when they build up to sufficiently high concentrations, they can cause building-related illnesses. Bio-based insulation materials can afford satisfactory thermal conductivity at a smaller environmental footprint than conventional insulation materials. There is an increased chance for VOC emissions, when biomaterials with intrinsic carbon-based chemical structure are used. The purposeful use of bio-based insulation materials, including hemp-lime mixes, wood fibre board, cellulose flakes and sheep's wool, to reduce the total volatile organic compound (TVOC) emissions in components of toluene, and formaldehyde separately, was studied (Maskell et al. 2015).

Individual VOCs were largely unsaturated hydrocarbons, aldehydes, acetic acid and alcohols. Wood fibre sample emitted high concentrations of acetic acid and furfural. Hemp-lime mixes emitted but-1-ol. Wood-based materials, without adhesive resins, emitted formaldehyde due to oxidative, thermal, enzymatic and microbial degradation of the wood-based material (Mittal et al. 2017). Wood fibre-based insulation exhibited emission rates giving rise to concentrations in air of up to 607 μg m^{-3} TVOC and 13 μg m^{-3} formaldehyde. The VOC quenching by wool due to the reaction of amine groups of lysine and arginine and the amido groups of asparagine and glutamine with organic compounds such as formaldehyde is the reason for air purification, increasing indoor air quality (Baumann et al. 2000).

3.6 Sound Insulation Barrier Property

Noise reduction and noise control are essential considerations in modern urban construction, for fulfilling health and safety guidelines and reducing the impact on surroundings. The alternative, sustainable materials to replace asbestos-based and synthetic fibre-based sound-absorbing materials with the improved application is an area of widespread research, since the late 1990s. Natural fibres with lightweight, porous internal structure, containing a network of air cavities, in their hollow cell lumens, allow attenuation of sound energy by multiple mechanisms compared to the solid glass fibre. Sound absorption coefficient increases with a decrease in bamboo fibre diameter, as the number of fibres increases for the same cross-sectional area (Koizumi et al. 2002). When sound waves are incident on the natural fibre, the transmission into the fibre lumen with multiple pathways would cause loss of energy, along with conversion to heat, due to friction. The vibration of air in the lumen and bulk leads to fibre vibration. These pathways explain the excellent sound-absorbing coefficients of the fibre structure. Natural fibres are processed in a one-step cold/hot compacting with resinous fibre bonding agents to produce low-density and hot-pressed higher-density, one layered structured composites. With bamboo and kapok fibre, sound absorption coefficient increases with density, but an optimal sound-absorbing fibre mass density exists. Also, the higher the sound frequency, the shorter the wavelength, and the longer the propagation of sound waves in the network structure of the composites, causing greatest dissipation, producing best sound absorption performance at high frequencies. The different kinds of composites, which have been studied for sound absorption capability, are ramie, flax and jute composites with epoxy glue, corn particle board with wood glue, kapok fibre blended with polypropylene, hemp concrete, coconut fibre composite, tea-leaf fibres with polyurethane blend, rice straw-wood particle composite with formaldehyde resin, etc. (Zhu et al. 2013).

Activated carbon fibre composites, with the ACF non-woven structure blended along with fibres, allow greater air capacity to absorb sound. Addition of inorganic particles like precipitated calcium carbonate increased the stiffness of the composite while adding to the sound absorption. This was also seen in kenaf rubber composites containing calcium carbonate. Rigid, lightweight sound-absorbing materials can be generated from natural fibre sources, though their other properties such as fire retardancy may have to be improved. Multilayered structures such as sandwich structure and honeycomb structure have also been used to improve sound and vibration damping compared to synthetic fibre sandwich panels. Natural cork bundle as core covered with carbon fibre top sheets in sandwich form has exemplary sound absorption. Balsa, pinewood and synthetic foam as core with natural fibre composites as surface layers in the sandwich have low shear modulus cores matching structural damping values. Nano-fillers in composite mixes are another solution to achieve target properties of sound absorption with shading, insulation, moisture barrier and mechanical strength (Zhu et al. 2013).

3.7 *Optical and Conductive Property*

Biochar is produced from the thermal decomposition of biomass in the absence of atmospheric oxygen wherein fast pyrolysis process produces a solid residue (char), liquid condensate and gas products, while slow pyrolysis process produces carbonization to biochar/charcoal. They have been used as substitute electrode material as anode and cathode in microbial fuel cells, with comparable performance output, to activated carbon and graphitic granules (Huggins et al. 2014). Resistivity measurements showed that the biochar material, derived from high-temperature treatment of waste wood at 1000 °C, was highly conductive with a resistivity of $3.1 \pm 1\ \Omega\cdot\mathrm{cm}^{-1}$. Increased treatment temperature produces a graphitic structure, with volatilization of dross organic matter. Biochar particle-filled (8%, 10%, 12%) PVA films possess suitable electrical conductivity and piezoresistive response and would be likely materials for piezoresistive sensors. The voltage output of the biochar/PVA sensor was highest for the highest loading of biochar, and the piezoresistive response did not vary significantly with film thickness (0.4–0.5 mm). They also did not degrade in response with multiple pressing, i.e. they had good recovery capability, essential for a pressure sensitive sensor (Nan and De-Vallance 2014). The use of textile fibres and fabrics coated with conductive nanoparticles such as polypyrrole has been another pathway to bio-based conductive materials.

Biologically derived optically transparent materials can be transformed into optoelectronic materials (Nan and De-Vallance 2014). DNA films can be utilized to function as a combination of hole-transporting and electron-blocking layer in optical devices. The DNA composition and derived physical properties can be manipulated by sequence selection, chemical functionalization and physical manipulation, to obtain required films to produce multilayer white polymer organic light-emitting diode (LED). Further research in charge transport in biopolymers would extend applications to medical devices, sensors and flexible biodegradable electronics for timed usage in implants and healing.

4 Bio-based Materials for Functionality Packaging

Plastic has become the most-used packing material in food and textile for consumer durables. However, plastic is a huge problem precisely because of its durability, and it poses a huge threat to our ecosystem. Discarded plastic bags have been linked to major disasters. Reduce, reuse and recycle of plastics are not sufficient to minimize the environmental impact and health threats. There exist many numerous research findings that the chemical additives in plastics, such as bisphenol-A (BPA) and phthalates (which keep plastics soft and pliable), are causing harmful effects on human health. The processing of plastics not only releases a lot of heat but a huge amount of carbon dioxide (Muneer 2013). Paper as food packaging also has its limitations. Corrugated containerboard is used to ship and transport packages ranging from electronics to fragile glassware to perishable goods; paperboard packages food, medicine and toiletries for handy storage and display. Paper bags give customers a sustainable choice to carry their purchases home. Brick carton's complex composition makes it difficult to decompose. Glass is considered to be pure and safe material for packaging. But if the glass is used to package products, one should be ready for its brittleness and high processing cost. Large amounts of energy are expended in the production of traditional packagings like plastics, corrugated boxes and plastic bags. Frequently, the energy is derived from burning fossil fuels that release large volumes of greenhouse gases like carbon dioxide and methane into the atmosphere, while disposed conventional packaging gets dumped in landfills or oceans causing soil, water and plant pollution. Hence in order to avoid all these harmful effects, we need to resort to sustainable means of packaging.

Biodegradable polymers and molecules which rely on feedstock sources—from annually grown crops like wheat (wheat gluten), soy (soy proteins), corn and potatoes (starch), cassava and its waste, green coconut shell extract, sugarcane and hemp—give a foundation for sustainable and eco-efficient products which can substitute and supersede plastics and composites made mainly from the petroleum-based feedstock. Bio-based materials maximize the use of recycled and renewable materials and low-impact production processes, thereby conserving raw materials. Conserving raw materials, in turn, preserves natural resources. Also, bio-based materials minimize exposure to potentially toxic and hazardous chemicals. Bio-based materials introducing eco-friendly and biodegradable product (cloth, paper and jute bags) are generally used in all shops for packaging and carrying items (refer Fig. 4).

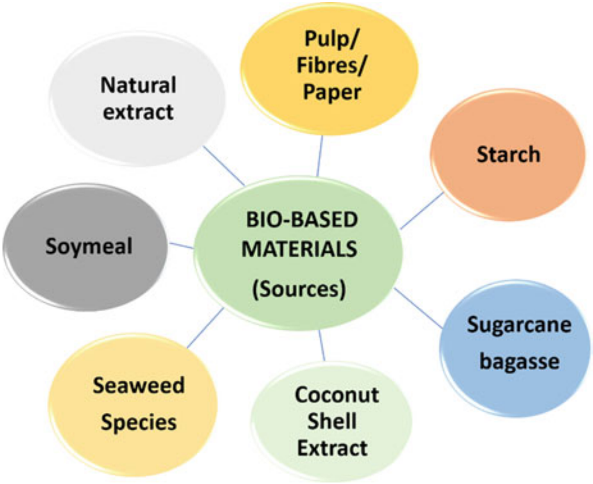

Fig. 4 Natural sources of bio-based materials

4.1 Bio-based Materials from Starch

Different glycerol contents were used for plasticizing the starch films. Cassava starch has been comprehensively used to make biodegradable films which feature non-toxic, isotropic, odourless, bio-degradable and colourless characteristics. Tree cassava films possessed better water solubility and water vapour permeability relative to those of cassava films irrespective of glycerol content (Souza et al. 2012). Scientists presented a study in which the effect of glycerol content and its blending method on barrier and tensile properties of biodegradable films from cassava starch were investigated. The influence of nano-clay particles and glycerol on tensile, barrier properties and glass transition temperature of biodegradable films produced from cassava starch was studied. The results established that films made from plasticized cassava starch reinforced with clay nanoparticles were appraised favourably as bio-based packaging material (Souza et al. 2012).

A review focused on properties of starch and sugar palm fibres and their products in green composites. The review also revealed the prospects of sugar palm fibres and biopolymer for industrial applications such as automotive, packaging, bioenergy and others (Sanyang et al. 2016).

Studies on the means and methods to prepare and characterize some polyvinyl alcohol and starch polymeric blends have been done. Polyvinyl alcohol (PVA) is positioned as the few biodegradable synthetic polymers that are easily and often modified owing to their properties. PVA dissolves easily in water as it contains multiple polar alcohol groups and may form hydrogen bonds with water. Starch, functioning as a storage polysaccharide in plants, is a frequently used biopolymer. It constitutes both linear and branched polysaccharides, like amylose and amylopectin. Starch is one of the most widely available and inexpensive polysaccharide sources which have the unique characteristic of “biodegradability”, and it can be easily decomposed in water. It was seen that as content of the starch in PVA/starch blends increased, the melt processing characteristics reduce. It was observed that there was an increase in the melt viscosity of polyvinyl alcohol/starch blends with the increase of starch content which indicated a hard processability during mixing. Films containing starch showed lower UV transmittance compared with PVA/glycerol sample indicating that polyvinyl alcohol/starch films are a good defence against ultraviolet light. The moisture permeability of tested samples increased proportionally with the addition of starch. The results derived from experiments showed that the polymeric material made from polyvinyl alcohol and starch had favourable physical-mechanical characteristics, being suitable for packaging industry (Tănase et al. 2015).

The degree to which chemical structure of high-amylose maize starch films and its functional properties were influenced by temperature and time during the manufacturing process and the level of plasticizer content was examined. The films were prepared from a slurry of high-amylose maize starch and water (2.2 or 2.6 g/100 g water) that was heated in an autoclave and mixed thoroughly. The influence of variable film-forming conditions on its cohesiveness was compared. The strongest film was the non-plasticized. But glycerol was required to obtain films that were cohesive. Tensile strength was most affected by glycerol content, one of the processing factors. Longer heating times and hotter processing temperatures made films that were not contiguous but fragmented. Such stressful processing conditions caused starch degradation and brittle film. The temperature was more significant than time in influencing the progress of starch degradation. High molecular weight amylopectin and amylose were more likely to undergo thermal degradation. The aggregation of starch molecules in a definite microstructure through different stages of film formation to a final macrostructure was unfavourably affected by degradation. However, there were no similar changes in the mechanical properties with longer processing time or increasing heating temperature (Koch et al. 2010).

4.2 Bio-based Materials from Coconut Shell Extract

The multifunctional effect can be obtained from green coconut shell extract (CSE) applied on jute (lingo-cellulosic), cotton (cellulosic) and wool (proteinous) which can be a good low-cost bio-based packaging material. Application of CSE at different pH on these materials enhanced the thermal stability of the jute, cotton and wool fabric. Flame retardancy in the CSE-treated jute, cotton and wool fabric might be ascribed to the presence of inorganic metal salts, phosphate compounds, phenolic groups, etc. which promoted the production of foaming char which acted as a protective barrier and decreased volatilization and the formation of combustible gases. On jute and cotton fabric, CSE application was carried out in acidic, neutral and alkaline pH where as in wool it was carried out only in acidic pH 4.5 (as is extracted). Moreover, the inherent strength of jute, cotton and wool fabric was preserved. Treated jute and cotton fabric exhibited superior antibacterial property and very good ultraviolet protection properties. Moreover, treated jute, cotton and wool fabric showed inherent natural colouration, and it was found to be more intense at higher concentration. Therefore, CSE acts as multifunctional bio-based sources for jute, cotton and wool materials which can be used for various sustainable packaging materials. The raw material of the green coconut shell is widely available as waste product, and this kind of application leads to good low-cost value addition for bio-based packaging materials (Teli et al. 2017a; Teli and Pandit 2017a, 2018). Similarly, other natural sources such as banana pseudostem sap, *Sterculia foetida* fruit shell extract, *Delonix regia* stem shell waste, peanut husk, herbal-synthesized particle, etc. have been used by our research group on natural fibres as bio-based packaging materials (Teli and Pandit 2017b, c; Teli et al. 2017b; Basak et al. 2016; Pandey et al. 2018).

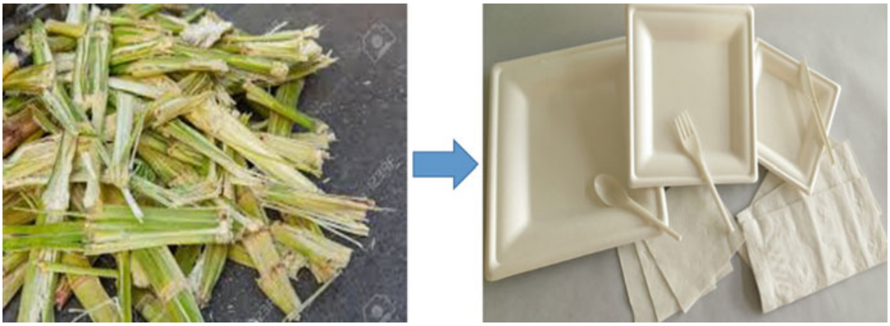

Fig. 5 Different products made from sugarcane bagasse

4.3 Bio-based Materials from Sugarcane Bagasse

Sugarcane bagasse cellulose was subjected to a homogenous chemical modification of esterification using phthalic anhydride reagent providing the acidic groups for esterifying the hydroxyl groups. The successful transformation to sugarcane bagasse phthalate films (considered a bioplastic) was achieved as proven by the absence of cracks or collapse in films obtained on drying after solution casting using DMF solvent. The sugarcane bagasse phthalate films displayed a uniform and consistent three-dimensional structure of their component polymeric chains. Increasing esterification however reduced the tensile strength of sugarcane bagasse phthalate films, with increasing weight percentage gain. A satisfactory breakthrough would be to obtain increased film flexibility while retaining strength in a bioplastic equivalent or better than in a natural banana leaf (refer Fig. 5) (Chen and Shi 2015).

4.4 Bio-based Materials from Variety of Seaweed Species

An in-depth review of a variety of seaweed species and seaweed products was done with a focus on the use of bioresource in the pharmaceutical industry and mostly applied in the medical field. Marine algal seaweed species are a bioresource, which has not been utilized to its maximum potential. Seaweeds are notable for the natural polysaccharides that can be extracted from them which are widely used in the area of biotechnology, microbiology, food technology and medicine. Carrageenan, agar and alginate are some of these polysaccharides. Since they are renewable biomass resources and are polymers of carbon chains composed of sugars, bioplastics may be prepared from them (refer Fig. 6). Additionally, seaweed and products derived from it have been expansively employed as a crucial ingredient in numerous pharmaceutical preparations like tablets, as rate retardant in sustained and extended release dosage forms and as bioplastic in the packaging industry. Bioplastics from

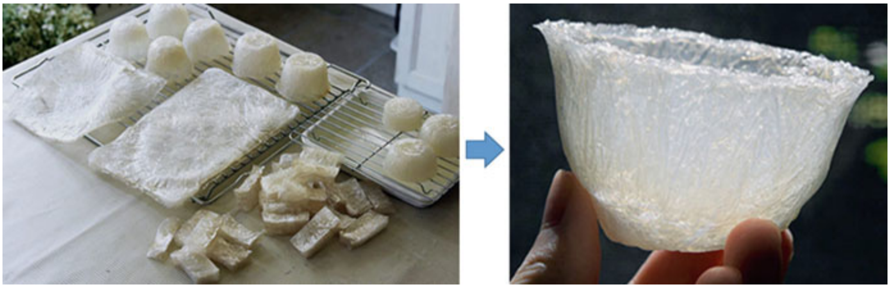

Fig. 6 Bioplastics from seaweed species

seaweed might be costly, but they have gained attention of late, because of their advantages over other biological sources (Gade et al. 2013).

Inexpensive and semi-refined kappa carrageenan, that is used as a seaweed polysaccharide in the preparation for strong biodegradable films, exhibited improved performance over conventional films. The formulation required no gelling salt, and the only other required additions to the film are glycerol and water. The films could be reprocessed and recycled if required (Meena et al. 2011).

4.5 *Bio-based Materials from Soymeal*

An attempt was made to use low-priced soymeal (SM) in place of costlier purified soy protein isolate and soy protein concentrate, as the raw material for manufacturing biodegradable and bio-based sustainable film. This required study of some of the modified initial processing steps, such as fermentation of soybean meal, the starting material, to dismantle some of the carbohydrates components while retaining the value of plasticizing ingredients (protein and pectin). Simultaneous saccharification and fermentation (SSF), yeast fermentation (YF) and natural fermentation (NF) were some of the multiple modes of fermentation process involved. Such fermentation degraded soymeal that was then plasticized with glycerol and then further blended with poly (butylene adipate-co-terephthalate) (PBAT); optimization of the proper mixing of plasticized soymeal with poly (butylene adipate-co-terephthalate) was done to better the performance of the resulting composite. Simultaneous fermentation and saccharification were found to be of benefit in function. The disadvantageous performance of proteins was overcome by their blending with other biomaterials in a cheap, efficient manner. The cost-efficient films so developed could have applications where biodegradable films are usable such as in consumer bags, packaging films, silage wraps and agricultural mulch films (Mekonnen et al. 2016).

Soybean-based fibre is a regenerated protein fibre, which may be blended with PVA, PE, nylon, cellulose, PP, PLA, PHA, etc. It is nonallergic, biodegradable and micro-biocidal. Soybean fibre itself is made from soybean cake after oiling by a bioengineering process. This involves, first, the distillation and refinement of spherical protein from soybean cake; the spatial structure of the spherical protein is then changed under the action of biological enzymes and auxiliary chemical treatment; after the liquid material is cooked, the 0.9–3.0 dtex fibre is generated by wet spinning, stabilized by acetalizing and lastly cut into short staples after curling and thermoforming. Fabrics produced from this have a good handle, draping property, moisture absorption and air permeability along with colour fastness, acid/alkali and light resistance, suitable for premium clothing. It may be blended with cotton, wool, polyester, etc. Chemical modification of soybean fibre during processing of the soybean protein meal could involve various routes to cross-linking, internal plasticization and compatibilization with hydrophobicity enhancers and/or blend with suitable resins to obtain favourable properties (Kumar et al. 2009; Guerrero et al. 2014; Vieira et al. 2011; Su et al. 2010).

4.6 Bio-based Materials from Pulp/Paper/Fibre

The production of paper was carried out wherein the main raw material for paper production that is pulp was obtained from the banana plant. This pulp could be blended with pulp obtained from bamboo which is less abundantly accessible to obtain oil-proof paper. The motivation behind the choice of banana as a raw material was that in banana plantations, after the fruits are harvested, the trunks or stems are discarded. Billion tons of stem and leaves are thrown away annually. In this project, pulp was produced from the banana waste stem by means of soda process and kraft process; also analysis of both processes based on their energy and raw material consumption yield was done, and a most efficient process was delivered (refer to Fig. 7) (Marella et al. n.d.).

The development of coatings and films, based on proteins, included suitable application in board or paper products, as well as prospective industrial potential. The signatory amide-based chemical structure of proteins gives rise to various properties but most significantly a high intermolecular binding potential such that protein-based films exhibit much improved mechanical properties than polysaccharide- and fat-based films. Two main types of generating protein coatings could be used: a wet process based on dispersion or solubilization of proteins, subsequently taken for drying, and a dry extrusion process based on the thermoplastic properties of proteins. Other processes using chemical transformation and cross-linking of proteins were also frequently utilized for modulating mechanical, barrier, surface and biodegradable properties (Coltelli et al. 2015).

Fig. 7 Bio-based materials from pulp/paper/fibres

4.7 Bio-based Materials from Sodium Alginate and Chitosan/Chitin

L-Guluronic acid and D-mannuronic acid are the two component monomer units which form the polymeric macromolecule of sodium alginate. Alginate fibres are used in commercial wound dressings as they resorb wound exudate while being a barrier to external infective agents sustaining a favourable microenvironment for tissue regrowth. Calcium alginate is prepared by reacting aqueous sodium alginate with the added aqueous calcium chloride. Chitin and chitosan may be considered as cellulose-like polymers in that the C-2 hydroxyl group of the ß-glucose monomer component is substituted with an acetamido group in chitin, while it is substituted with an amino group in case of chitosan. Based on the understanding of this chemical structure, removal of the acetyl group in the substituent produces the chitosan. Chitosan, having large-volume industrial utility, has a chemical structure composed of glucosamine units linked by 1–4 glycosidic bonds to N-acetyl glucosamine units. Being biocompatible, biodegradable and non-toxic gave it huge applicability in different industrial products such as those from food, biomedical, cosmetics, agricultural, textiles, pharmaceutical industries (Raafat and Sahl 2009).

5 Functionality of Bio-based Materials from Biopolymers

The key qualities of healthcare products include antiviral, bacteriostatic, non-toxic, fungistatic, high absorbent, nonallergic, breathable, haemostatic, biocompatible and ability to incorporate medications while also possessing reasonably good mechanical properties. Rigid packaging, flexible packaging, textiles, agriculture and horticulture (soil retention sheeting, agriculture film), non-woven fabrics for agriculture, filtration, hygiene and protective clothing are some such products. The production of biopolymers is increasing continuously from 1.5 million tons in 2012 to likely reach 6.7 million metric tons by 2018 (Johanson and Vahlne 1977). A few important biopolymers are discussed.

5.1 Polylactic Acid (PLA) and Bio-polyethylene

PLA, discovered in 1845, is the only melt-processable fibre from annually renewable natural resources such as cornstarch, tapioca or sugarcane. The process of its manufacture involves the extraction of starch from the raw natural plant source. The starch is degraded to its monomer dextrose and taken for fermentation without prior purification. The fermentation products are the D- and L-isomers of lactic acid, which is taken as the base monomer for preparation of mesolactide and final PLA polymer production. PLA is subsequently modified, as required, and drawn into fibres, cast as films or moulded into plastic products like bottles. The favourable properties of the bioplastic, PLA fibres are strong and durable, and their fabric has good drape and UV resistance. The limiting oxygen index (25) is higher than that of PET. It has low water uptake (0.4–0.6%) but greater than that of PET and PP (Douka et al. 2017; Choudhury 2018). Bio-based polyethylene has identical physical, chemical and mechanical properties to petrochemical polyethylene. The biological method of production involves an initial fermentation of sugarcane or other plant starches to bioethanol, which is distilled at high temperature over a solid catalyst to reduce it to ethylene monomer. This is then polymerized by microbes or a green polymerization to polyethylene (Choudhury 2018).

5.2 Poly(Alkylenedicarboxylate) Polyesters and Bacterial Polyesters

Common dicarboxylic and diol monomers found in poly(alkylenedicarboxylate) polyesters include succinic acid, adipic acid, ethylene glycol and 1,4 butanediol. They are used along with polyurethanes in the making of coatings, adhesives, flexible packaging, agricultural films and compostable bags, with other bio-based polymers to improve properties (Douka et al. 2017). Polyhydroxyalkanoates are biopolymers, which can also be produced biochemically by genetically modified microorganisms or plants. Polyhydroxyalkanoates can also be generated from glycerol, algae or aromatic sources likes plant lignins and tannins. Polyhydroxybutyrate copolymer named "Biopol" was developed by Zeneca Bioproducts (Choudhury 2018; Blackburn 2009).

6 Conclusions

Bio-based materials are significant because they decrease the ecological footprint at all the stages of the product's life cycle. Our exponentially increasing population and the global spread of economic development are both putting a demanding squeeze on the world's resources. The food, textile and plastic packaging industry have gained visibility in the forefront of the sustainability agenda, not because it is a major cause of environmental problems but because consumers are directly affected by their usage. Bio-based products became more attractive, and recycling of bio-based materials could be more sustainable than composting as a terminating procedure. Process development to tailor the physico-chemical properties of bio-based materials to their specific end application is an important tool, such as cross-linking matrix to increase mechanical strength. It is worth noticing that even if at the current stage of knowledge these materials look like a tiny compromise between sustainability and economic efficiency, the development of genetic tools allows hope in further full bio-based versions of these materials. Recent breakthroughs also concern the development of pure bio-based products identical to the petroleum-based materials.

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