Agro-Waste Valorization into Bio-Plastics: A Systematic Review of Types, Synthesis, and Characteristics

Verla Andrew Wirnkor[1], Maduabuchi Valentine Ibe[1], Verla Evelyn Ngozi[2], Olorunfemi Ebenezer Bola[1], Ejiako Joel Ejikel[1], Mkposong Stephen Asuqu[1], Iheoma Ezichi Mbuka-Nwosu[3]

[1]Department of Chemistry, Imo State University Owerri, P. M. B 2000, Imo State, Nigeria

[2]Department of Environmental Technology, Federal University of Technology, Owerri, Imo State, Nigeria

[3]Department of Environmental Management, Federal University of Technology, Owerri, Imo State, Nigeria

Abstract

Plastics,in as much as they play relevant roles, are undeniably one of the most prominent pollutions our planet suffers over the past couple of centuries especially due to their poor degradability and poor recycling, as it is obtained that a very huge amount of plastics produced over the past century are still present somewhere here on earth most likely as pollutants rather than in actual use or recycle. This work hence looks into a very much viable substitute to these plastic products which is bio-plastics, their types, unique and varying properties, also especially how they can be easily and economically obtained from a cheap raw material source such as agro-wastes which would otherwise have been deposited as wastes in rivers and other unsuitable places. The study goes on to show the basic monomer builds of the bio-plastic polymers which are obtainable from these wastes, comparing some of their basic properties like; Tensile strength, glass transition temperature et . It also enlightens on the various areas where these bio-plastics have potential tangible applications and also where they are already in use. It also goes on to emphasize especially the improvements that need to be put in place in order to encourage the speedy inclusion of these safer products into our everyday society which can be both enacting of laws to support and also concentration of research and technology into the development of the already existing knowledge and progress in the bio-plastic industry.

Keywords

Plastics Pollution, Bioplastics, Waste Valorization, Tensile Strength, Glass Transition Temperature

1. Introduction

Bio-plastics can be defined as biodegradable plastic that is made from biological materials [1].They are useful plastic materials which are produced from renewable biomass sources, such as vegetable, fats and oil, corn starch, straw, woodchips, sawdust, recycled food waste etc, rather than fossil sources. Some are obtained directly from natural biopolymers including polysaccharides (e.g soy protein, gluten and gelatin), while others can be synthesized chemically from sugar derivatives e.g lactic acid and lipids from either plants or animals or biologically generated by fermentation of sugars or lipids [2].

Due to growing environmental concerns, bio-plastic is a growing industry that is envisaged to replace regular plastics which has become a huge threat on the planet. Plastic is the third most commonly used petroleum derivative in the world, so apart from being contaminating to the environment and being non-biodegradable (taking more than 1000 years to decompose) it is also a problem as it comes from a non-renewable source (petroleum). This is why many countries such as Bangladesh and etc have put prohibitions on traditional plastic bags.

While conventional plastics are undeniably useful and sometimes necessary for many business and industrial uses, it is paramount that there should be a shift towards a more sustainable alternative for single use items like packaging. Especially noting that plastic waste, despite being a huge threat, it has had over nine billion tons produced since 1950's and only about 9% of it gets recycled. Every piece of plastic that was made in the last century is still present somewhere on earth, meaning that we have a large amount of plastic waste and is not going away anytime soon [3].

This is why in recent years, research and interest has been shifted to the normalization of the manufacture and usage of bio-plastics in our everyday life, especially for one-time uses, like packaging.

2. Methodology

The meta-analysis was carried out using specifically peer-reviewed journal articles published between the years 2013 and 2025, sourced from databases such as ScienceDirect, Scopus, and Google Scholar. The inclusion criteria required that studies specifically addressed the production of bio-plastics from agro-waste materials, including characterization data. Data were extracted on plastic type, feedstock used, synthesis method, chemical composition, mechanical and thermal properties, and biodegradation performance.

3. Types of Bioplastic

Bio-plastics include a wide and growing range and categorization of biological material based polymers that all possess unique attributes and uses. With new inventions constantly happening in the field due to continuously growing interest and research, the list is constantly growing.

3.1 General Categorization

Bio-plastics are usually categorized into three main groups:

Bio-based Plastics: this consists of bio-plastics made out of bio-polyesters e.g polyethylene (PE), polyethylene terephthalate (PET), certain polyamides (PA) etc.

Bio-based and biodegradable plastics: this consists of versions like polylactic acid (PLA), polyhydroxyalkanoates (PHA), polybutylene succinate (PBS).

Fossil-based but Biodegradable Plastics: these include polycaprolactone (PCL), polybutyleneadipate terephthalate (PBAT) [4].

3.2 Categorization Based on Biopolymer Make Up

However, below are the most common bio-based plastics being used in the present day, categorized based on their bio-polymer makeup along with some of their uses and applications

Starch-based Bio-plastic: These simple bio-plastics derived from corn starch, potato starch etc. they are sometimes often mixed with biodegradable polyesters in order to enhance the properties of the bio-plastics.

Starch-based bio-plastics are generally the most widely used raw material for making bio-plastics, they are used in the pharmaceutical industry for the production of capsules, and some companies have also successfully developed cellphone cases from compostable starch-based bio-plastics.

Additionally, they are often blended with other bio-polyesters in order to create high strength bio-plastics that can be used for commercial applications. Starch-based bio-plastics are also considered cost efficient since the raw, i.e starch, is cheap and abundant in availability.

Cellulose-based Bio-plastics: These are bio-plastics that are created by using cellulose esters and cellulose derivatives. They are used in the production of thermoplastics, extruded films, eyeglass frames, electronic sheets, rods, molding materials is also the most dominant application segment for cellulose plastics and the trend is expected to continue. Cellulose is also added to starch to create bio-polymers that have enhanced mechanical properties and are also highly water resistant [5].

Protein-based Bio-plastics: These are produced using sources such as wheat, gluten, casein and milk [6]. These protein based bio-plastics have become a leading alternative for food packaging as there has been major advances in protein based films and coatings for food packaging made from plant and animal proteins [5].

Bio-derived Polyethylene (PE): These are also known as organic polyethylene, they are usually produced from the fermentation of raw materials from agricultural products like sugarcane, corn etc.

Ethylene which is the monomer for the creation of the polyethylene, can be derived using ethanol and other fermented wastes from agricultural products. Hence the bio-plastics formed from the process is similar in chemical and physical properties to conventional polyethylene [4].

It is applied in several packaging materials such as crates, bottles for milk and fruit juices, jerry can, caps for food packaging etc.

Aliphatic Polyesters: These are various types of bio-based polyesters which are all together known as aliphatic polyesters. They are all more or less sensitive to hydrolytic degradation and can be mixed with other compounds. They include:

- Poly-3-hydroxybutyrate (PHB) ii) Polyhydroxyalkanoates (PHA)
- Polyhydroxyhexanoate (PHH) iv) Polylactic acid (PLA) v) Polyamide$_{II}$ (PA$_{II}$)

These aliphatic polyesters and other bio-polymers have many applications in medicine and pharmaceutical technology such as in drug delivery systems, wound closure, surgical sutures, implants and tissue engineering. In current day, there are many manufacturers of these aliphatic polyesters [6].

4. Bio-Plastic Production Methods

More generally the bio-plastics are produced via the following methods;

- Extracted directly from biomass e.g; starch, cellulose, gluten etc.
- Produced by natural or genetically modified organisms e.g; polyhydroxyalkanoates (PHA).
- Synthesized from biobased monomers e.g; polylacticacide (PLA), polyglycolic acid (PGA).
- Synthesized from petrochemicals e.g; polyvinyl alcohol (PVA).
- Produced by combining technologies and polymers e.g; starch-gluten blends [7].

5. Bioplastics Synthesis Methods

Generally, the synthesis of bio-plastics from agro-waste depends on the chemical composition of the feedstock and also the properties that are desired of the end-product.

Fermentation Processes: in this process, microbial fermentation is commonly used for the production of monomers like; lactic acid or polyhydroxyalkanoates. Bacterial strains such as Lactobacillus spp. and Cupriavidus necator are employed in converting sugars into polymers [8].

Thermoplastic Processing: in this case, starch and cellulose are processed through melt extrusion or solution casting. Plasticizers such as glycerol and sorbitol can also be added to improve flexibility [9].

Chemical Modification and Blending: agro-waste polymers are often chemically modified through esterification in order to enhance mechanical and thermal performance, acetylation, or cross-linking. Composites are also formed by incorporating nanoclay, lignin, or natural fibers [10].

6. Chemical Composition of Agro-Waste Feedstocks

The various agro waste that has potential to be used as bioplastics are bagasse, corn cob, cellulose, sago pith waste and chitin and they mostly compose of the following;

- **Cellulose (40-60%):** Offers strength and film-forming ability.
- **Hemicellulose (20-35%):** Provides flexibility but is less stable.
- **Lignin (10-25%):** Enhances rigidity and UV resistance.
- **Starch and Sugars**: Easily fermentable substrates.
- **Proteins and Oils:** Act as plasticizers or emulsifiers [11].

7. Key Bioplastic Raw Materials Obtained from Agro-Waste, Properties, Production and Applications

Having been established that bio-plastics are more generally obtained from biomass and hence usually food items, the first generation of bio-based polymers were mainly consisted of polymers that were derived from agricultural feedstock such as potatoes, corn and other food sources of carbohydrate and starch [12]. In recent days and time, the focus has shifted because of the need to delve away from food based . With the significant breakthroughs in biotechnology and research, lignocellulosicbiomass which consists of organic waste, fatty acids, starch and cellulose has become the priorities in substrates for fermentation process to produce the polymers for the bio-plastic production, as this more reasonably achieves the overall aim of recycling because the raw materials sources are supposed waste materials from agriculture (agro-wastes)rather than actual food that could be used for consumption or other needs instead.

Hence, going further on this, an overview of some key bio-plastics raw materials which include starch, polylactic acid and chitosan which are derived from agro-wastes would be considered and discussed along with their preparation, properties and applications.

7.1 Starch

This is a white, granular, organic chemical that is typically produced by all green plants. It’s a soft white tasteless powder that is insoluble in cold water, alcohol or other solvents [13]. Starch is a natural bio-based polymer and is the second largest biomass produced on earth after cellulose. It consists of glucopyranose (i.e six-membered-ring glucose) monomers which are linked by α-1-4 bonds and α-1-6 bonds. Trace amounts of lipids, residues of protein and phosphorus also exist in starch. [13] The specific chemical structures, morphology and properties of starch mainly depends on the botanical origin and genetic background, hence leading to diversity of the application of starch in the different sectors.

Starch is available widely from various natural sources such as potato, corn, tapioca and wheat. Moreover, it does not only find use in the food industry but also finds essential use in many non-food applications such as; adhesive in paper industry, excipient or binder and plasma volume expander in the pharmaceutical industry, additives in constructions and raw material in plastic industry [14].

7.2 Properties of Starch in Bio-Plastic

Although, starch is a polymer which is made up of chains of amylose and amylopectin, it isn’t classified as a thermoplastic [15]. Hence, for it to be able to exhibit the kind of processing ability which the conventional synthetic polymer exhibits, it has to be plasticized using water, sorbitol or glycerol, then treated and sheared at high temperature [16]. The required temperature for processing of thermoplastic starch often ranges from 140-160^{o}C. Just like synthetic thermoplastic, this thermoplastic starch can be softened and hardened repeatedly into different shapes via heat and shear forces. It is also able to possess physical characteristics with regular conventional plastics used in food packaging industry in terms of transparency and odor [17].

Thermoplastic starch however, exhibit inferior properties because of its affinity towards water, and this limits its usage in many applications. It is hydrophilic and its moistures content is very sensitive towards changes in relative humidity of its surrounding atmosphere, even though it is insoluble in cold water.

On the other hand, starch granules swell and undergo gelatinization when they are heated in water. Although the temperature at which the starch granules begin to gelatinize (gelatinization temperature), depends on some factors which are; the source of starch, the amylose to amylopectin ratio and water content. It usually ranges from 2^{o}C for single granule and 4-10^{o}C for a complex starch grit [16].

The advantages of thermoplastic starch notwithstanding, it has unsatisfactory mechanical properties and long-term stability. [18] having that the mechanical properties of thermoplastic starch can be altered via the ratio of amylose to amylopectin [19]. The thermoplastic starch which contains higher amylose content has better performance in terms of tensile strength, elongation at break and gas barrier properties due to the high crystalinity of amylose [20]. Notably also, plasticizers alter the structure and performance of thermoplastic starch, reduces its modulus and tensile strength, but simultaneously improves the elongation at break [21].

7.3 Production of Starch Bio-Plastic

Research on starch for bio-plastic purposes is generally based on processing of thermoplastic starch and the blending of this thermoplastic starch with different synthetic polymers [16,22]. Although the problem with this research lies in the fact that they depend on starch gotten from food sources such as potato, cassava and corn starch for the production of the starch which in turn leads to the issue of food scarcity. Hence it is way more preferable to produce bio-plastic from starch gotten from agricultural wastes such as Sago, because by doing so, the problem of causing food scarcity and also reduction of carbon footprint of bio-plastics can be simultaneously solved [23].

Sago is a type of starch that is gotten from Rumbia tree, a tree which is largely found in Sarawak, Malaysia. More preferably, for the sourcing of starch for raw materials from agricultural wastes, there is the Sago Pith Waste (SPW) which is also a great source of starch obtained from the unwanted parts of Sago [23]. the SPW is a fibrous residue that is obtained during the extraction of sago starch from sago palm pith [24]. The starch is then removed from the sago palm pith by extraction processes of rasping the pith and washing it with water vigorously. This rasped pith is the SPW, and still possesses a high composition of sago starch granules in the range of 60wt%-80wt% [25].

Recall that the SPW would normally have been mixed with waste water and discharged into rivers and would have led to more water pollution. From data obtained from the Malaysian Statistics Department, the sago starch produced in 2011 alone is about 52,000 tons [26]. It is also obtained from reports that the SPW disposed in the state of Sarawak contains high amount of starch which is almost half of the total amount of starch imported to Malaysia. This indicates a large amount of normally waste material that can serve as valuable raw material for bio-plastic production [27]. Meanwhile, the microbial decomposition of the SPW disposed in the rivers causes drop in the quality of water and endangers the aquatic organisms. This is because the organisms could not have sufficient amount of dissolved oxygen in the water as the oxygen has been consumed by the SPW during its bio-degradation [28].

Notably also, SPW contains a high composition of starch that can act as matrix that holds reinforcing fibers, it is possible to plasticize it into the bio-degradable composite material with the absence of any synthetic to function as the binder. This makes it a unique material when compared to other fibrous wastes. Hence, SPW has the capacity to produce useful consumer products and can be processed for several processing techniques such as compression molding, injection molding and thermoforming [23].

7.4 Poly-Lactic Acid (PLA)

This is a popular polymer in the bio-plastic industry, also known as poly-lactide. It is an aliphatic polyester and a biocompatible thermoplastic [24]. It is a biodegradable polymer derived in the process where bio-activity of bacteria is used to convert agricultural products into bio-based monomers for polymerization. Lactic acid is basically a carboxylic acid and can be produced from the fermentation of dextrose, dextrose that can be derived from plant starch by bacteria [29].

The poly-lactic acid was discovered in the early 1800's by Pelouze who condensed lactic acid through a distillation process to produce low yield and low purity PLA and lactide of low molecular weight [30]. Although the fermentation method is more preferable due to its environmental friendliness, aside from this method, the lactic acid can also be synthesized through chemical methods of which the most widely used method is the hydrolysis of lactonitrile by strong acids which would produce racemic mixtures of D- and L- lactic acid.Oter chemical means also include hydrolysis of chloropropanoic acid, nitric acid oxidation of propylene, oxidation of propylene glycol and reaction of acetaldehyde, carbon(ii)oxide and water at elevated temperature and pressures [31]. Also the lactic acid can directly be converted to lactide via oligomerization reaction at the hydroxyl and carboxyl group.

7.5 Properties of Poly-Lactic Acid

Just like other thermoplastics, the properties of PLA varies with different molecular weight, annealing time and processing temperature [32]. Its properties also depend on the stereo-chemical nature of its monomers and their ratio which can affect the degree of crystallinity of its polymer. When cold, PLA is only partially soluble in solvents such as ethylbenzene, acetone, toluene and tetrahydrofuran, but highly soluble in these solvents when boiled. It is a slow crystallizing polymer and can be crystallized by slow-cooling, strain crystallized or annealing over glass transition temperature. Notable, all types of PLA are insoluble in water, some alcohols and alkanes [23].

Generally, poly-lactic acid is a thermoplastic of great strength and modulus. It has high tolerance over different types of processing techniques and conditions. Some other of its unique characters includes; a glassy appearance and good transparency [33].

PLA is also a potential alternative to conventional polymers such as polyethylene terephthalate (PET), polystyrene (PS) and polycarbonate (PC) for application in automotive, electronics and packaging due to their similar mechanical properties. Its thermal properties however, especially glass transition temperature are inferior, this problem can be overcome by altering its stereochemistry or blending it with other polymers or processing aid.

7.6 Production of Poly-lactic Acid

The economics of production of lactic acid and its derivatives significantly depend on the cost of raw materials [34].

Because of this cost of the raw materials, the preferable usage of agro-waste and residues as an alternative source to replace the costly raw materials has been the main challenges in the large scale production of the lactic acid, especially in the bio-plastic industry [35,36].

For the production process, it was learnt that the usual double step fermentation process to produce lactic acid can be replaced by simultaneous saccharification and fermentation. The saccharification of starchy or cellulosic biomass and conversion to lactic acid can occur concurrently by adding inoculum along with substrate degrading enzymes. This simultaneous process both lowers the PLA production cost and also improves the productivity by supplying adequate sugar release [37]. Bacteria with amylolytic and lactic acid producing characters can directly convert starchy biomass to lactic acid and make the process economical [38].

The most popular cheap raw materials that have been used for lactic acid production include starchy and cellulosic materials, where different micro-organisms are used for the different preferable types of lactic acid to be produced [37] one of the main sources of this starchy and cellulosic raw materials is cassava, which is a very important food crop and a large part of it is commercially used to obtain starch. Hence, in order to be more conservative and economically viable, the bio-plastic application does not depend on the main cassava product but rather on the waste by-product in the form of bagasse which is the solid residue gotten from its industrial application [39]. Large amount of starch was found trapped in this cassava bagasse fibrous matter making it a worthy replacement.

Another main source of the starchy and cellulosic raw material is sugarcane bagasse, which contains about 50% cellulose, 25% hemi-cellulose and 25% lignin, and it is also the major by-product of sugarcane industry [40]. it is very abundant, and because of this it can ideally serve as substrate for microbial process for the production of value added products such as bio-plastics. Brazil which is a country with its economy majorly based on agriculture fully explored the potential of sugarcane. In the years 2015-2016, 666millions of tons of sugarcane were produced and for each ton 250-270kg of bagasse was obtained [41].

Other agricultural residues with great potential as low cost substrate for production of PLA include corn hub, processed wood waste and empty fruit bunch (EFB) from oil palm trees [23].

In the bio-plastics market data 2018 report by European Bio-plastics, PLA accounted for approximately 10.3% of the global bio-plastic production capacities [42].

PLA has its main role in many sectors such as packaging, agriculture, textiles, transportation and electronics. In these sectors, packaging alone contributed to the largest segment of 35.7% of volume based share in the overall industry as at 2017. In packaging, PLA finds its applications as bottles, containers, flexible packaging and labels. In electronics sector it has so farbeen limited to the development of CD-ROM, cases and SD-cards. In agriculture, it is used for mulch film to regulate the release of pesticides and fertilizers. PLAalso shows great growth in its potential for textile industry as it can provide smooth fabrics with excellent ultraviolet (UV) and moisture resistance, low smoke formation and flammability. It can also be used in body care products, creams and shampoos. Meanwhile the core focus of studies on PLA and its co-polymers in biomedical applications are in bone and tissue engineering, drug delivery system, wound treatment and medical implants which include pins, screw, rods and plates [23].

7.7 Chitosan

This is a cationic polysaccharide with high molecular weight and is derived by deacetylation from chitin via alkaline treatments. It is composed of N-acetyl-D-glucosamine (acetylated unit) and β-(1,4) linked D-glucosamine (deacetylated unit) that is distributed randomly [43]. It is a fibrous substance and a sugar which comes from the outer skeleton of shellfish, including crab, lobster and shrimp [44]. It is the only polycation in nature, termed valuable because of its abundance,properties and diverse applications. In 2019, the global chitosan market was sized at USD6.8 billion, and is expected to expand significantly in consequent years [45].

7.8 Properties of Chitosan

Chitosan is insoluble in water and alkaline solution but is soluble in dilute acid solutions [46]. This is attributed to the protonated amino groups that are present in its molecules.This leads to the distribution of positive charges along its molecular chain ($-NH^{3+}$) [47]. It also possess weak permeability to oxygen and has very good film forming ability which makes it useful in food packaging as it reduces the respiratory rate of food [48]. It is a non-toxic material that possess excellent biocompatible and biodegradable properties, which gives it the advantage of preventing pollution to the environment when it is discarded as waste, instead it is able to improve the micro-ecological properties of soil [49].

Chitosan also exhibits intrinsic antioxidant and antimicrobial properties, these making it a widely used material especially in food packaging applications to extend the shelf life of vegetables, fruits and meats [50]. This its antioxidant capacity can be credited to the feasible reaction between residual free amino groups of chitosan with free radicals, which leads to the formation of stable macromolecular radicals and ammonium groups [51]. Meanwhile in explanation of the antimicrobial property, it is due to the interaction between the polycationic amino groups of the chitosan and the negatively charged microbial cell membranes which consequently increases the membrane permeability leading to cell deaths [52].

Unfortunately, there are some downsides to the properties of chitosan which has limited its applications from growing wider. Just like other polysaccharides, the films produced from pure chitosan has low mechanical strength, brittle nature and poor barrier property to moisture [53]. Consequently, this chitosan films are highly sensitive to water vapor, hence their usage in food packaging is totally limited to protein rich and unsaturated fatty acids rich foods, as well as in environments with high relative humidity.

Also, even though chitosan possess antimicrobial property, these antimicrobial activity are limited, hence the use of pure chitosan fails to satisfy market needs [54,55]. Generally, improvements are necessary on the antimicrobial and antioxidant properties in order to widen the applications in active packaging as the films made from pure chitosan fails to achieve the required standard [56].

Derivatives from chitosan have been made with the aim of improving its properties such as solubility and biodegradability, and also to introduce new functions or properties [57]. Also, in this era of nanotechnology, nano-composites of chitosan are produced with enhanced properties in order to widen the applications, especially in food packaging [58].

7.9 Applications of Chitosan Bio-plastics

Even though chitosan has a wide range of applications, chitosan-based bio-plastics more generally find use in biomedical applications. In this field, chitosan-based films finds use as catheter [59]. It is also used to coat surface of Polyethylene terephthalate (PET) and Polyethylene (PE) catheter because of its anti-adhesive and anti-bacterial abilities [60] It is also able to fulfill the requirements for the fabrication of contact lens, hence it finds application in this purpose and contact lens made from chitosan are clear, tough, possess sufficient physical properties (tensile modulus and strength, tear strength and elongation), wettability, oxygen permeability and importantly immunological compatibility [61].

Chitosan also finds use in the tissue engineering field as the biocompatibility of chitosan from shrimp and cuttlefish was investigated for cell adherence and growth by simply varying the percentage of deacetylation [62]. Research into this obtained that a high percentage of deacetylation of chitosan is able to increase its cell attachment, this is because, high percentage deacetylated chitosan have more free amino groups which can be protonated to form cationic amine groups and produce positively charged surfaces, thereby allowing the interaction between the chitosan surfaces and cells [62]. Hence, chitosan is becoming an attractive bio-material for fabricating bone scaffold and articular cartilage [63]. Chitosan scaffolds can be fabricated bulkily by different methods such as gas foaming, freeze gelation, particulate leaching and most popularly, the phase separation and lyophilization method [64].

8. Material Properties of Agro-Waste Bioplastics

8.1 Mechanical Properties

As illustrated in Figure 1, some studies have reported tensile strengths of bioplastics made with different starches to be as low as 1.67 MPa and as high as 28.35 MPa [65]. Tensile strength values typically range from 5-35 MPa, depending on polymer type and reinforcement. PLA and PHA composites exhibit the highest mechanical performance, For PLA, tensile strength varies from 39.9 MPa to 52.5 MPa [66]. Chitosan bioplastics on the other hand exhibited tensile strength ranging from 53.37 - 64.68 MPa. For conventional plastics, depending on the specific type of plastic and its reinforcements but the tensile strengths is generally from 20 - 100 MPa.

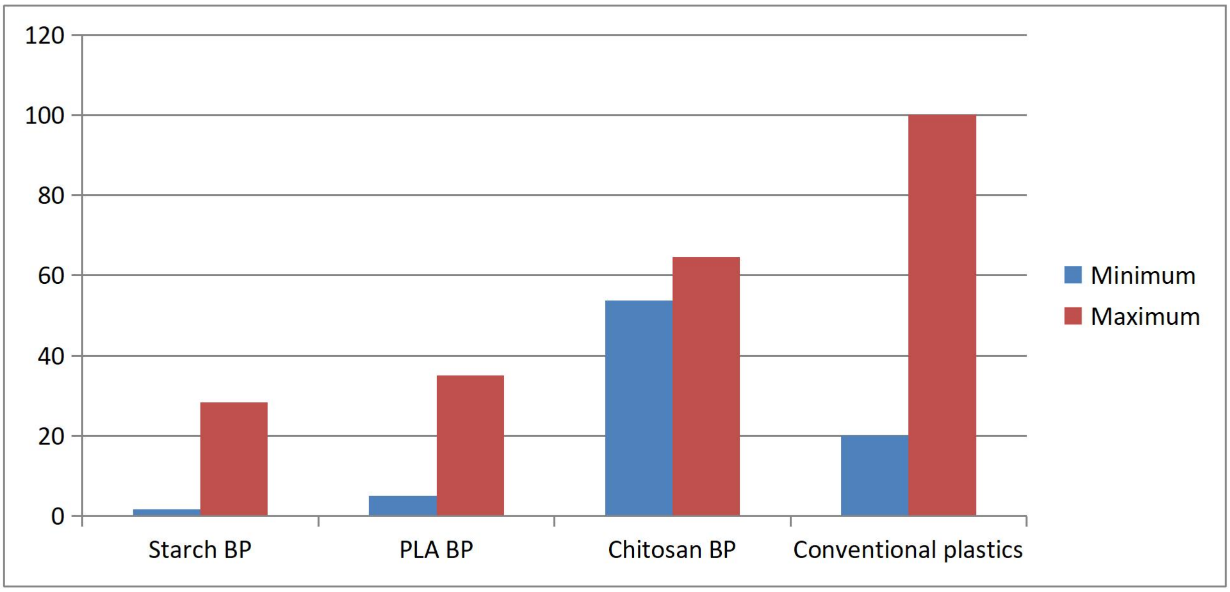

Figure 1. Bar Chart showing the minimum and maximum values of tensile strengths (in MPa) for the three major types of bioplastics

Tensile strength is a critical mechanical property that quantifies a material's resistance to breaking under tension. It is defined as the maximum stress a material can withstand before fracturing when stretched or pulled. In the context of packaging and other applications, high tensile strength indicates a material's ability to resist tearing, stretching, and breaking during handling, processing, and use, directly impacting its durability and protective capabilities.

The tensile strength values for various bioplastics demonstrate a wide range, highlighting the influence of polymer type, formulation, and reinforcement strategies:

Starch-based bioplastics: Reported tensile strengths vary significantly, from as low as 1.67 MPa to as high as 28.35 MPa. This wide range is largely attributable to the diverse formulations and modifications of starch, including the type of starch used, the presence of plasticizers, and the incorporation of reinforcing fillers. Unmodified starch films are often brittle and possess low tensile strength, necessitating reinforcement for practical applications.

PLA (Polylactic Acid) and PHA (Polyhydroxyalkanoates) composites: These bioplastics generally exhibit higher mechanical performance. For PLA, tensile strength typically ranges from 39.9 MPa to 52.5 MPa. This higher range, particularly when reinforced, makes PLA a competitive alternative for applications requiring moderate strength.

Chitosan bioplastics: Demonstrated even higher tensile strengths, ranging from 53.37 MPa to 64.68 MPa. This indicates that chitosan-based materials, especially when processed optimally or reinforced, can offer excellent mechanical robustness.

8.1.1 In Comparison with Conventional Plastics

When compared to conventional petroleum-based plastics, the tensile strengths of bioplastics show a varied landscape:

General Range for Conventional Plastics: Depending on the specific type of plastic and its reinforcements, tensile strengths generally range from 20 MPa to over 100 MPa. For instance:

Low-Density Polyethylene (LDPE): Typically has a tensile strength of 8-30 MPa, known for its flexibility.

High-Density Polyethylene (HDPE): Exhibits higher strength, often ranging from 20-40 MPa.

Polyethylene Terephthalate (PET): Widely used in bottles, it can have tensile strengths from 50-70 MPa, and even higher for oriented films (up to 200-300 MPa).

Polystyrene (PS): Offers tensile strengths of 35-55 MPa, known for its rigidity.

8.1.2 Analysis of Bioplastic Performance

Starch-based bioplastics often fall on the lower end of the spectrum for both bioplastics and conventional plastics, especially without reinforcement. Their mechanical properties are highly sensitive to moisture content and plasticizer concentration.

PLA and PHA composites, while generally better than basic starch, still typically operate within the lower to mid-range of conventional plastics. They are strong enough for many packaging and single-use applications but may require reinforcement or blending for high-stress scenarios.

Chitosan bioplastics stand out with tensile strengths comparable to, and in some cases exceeding, the lower to mid-range of conventional plastics like HDPE and PS, making them promising for applications requiring robust mechanical performance.

8.1.3 Factors Influencing Tensile Strength in Bioplastics

Several critical factors dictate the ultimate tensile strength of bioplastics:

Polymer Type and Chemical Structure: The inherent strength of the polymer chains, determined by molecular forces (e.g., hydrogen bonding, van der Waals forces) and chain entanglement, plays a fundamental role. For instance, the strong hydrogen bonding network in chitosan contributes to its higher strength.

Molecular Weight: Higher molecular weight generally leads to increased tensile strength as longer polymer chains can interlock more effectively, requiring more energy to pull them apart.

Crystallinity: For semi-crystalline polymers (like PLA, PHA, and some modified starches), a higher degree of crystallinity often correlates with increased tensile strength and stiffness due to the ordered, densely packed crystalline regions.

Plasticizers: The addition of plasticizers, used to improve flexibility and processability, typically reduces tensile strength by increasing free volume and decreasing intermolecular forces between polymer chains.

Reinforcement/Composites: The incorporation of reinforcing agents such as natural fibers (cellulose, lignin), nanofibers, nanocrystals, or inorganic nanoparticles (e.g., nanoclays) is a highly effective strategy to significantly boost the tensile strength and stiffness of bioplastics. These fillers can act as stress concentrators or form a load-bearing network.

Processing Methods: Parameters like film thickness, stretching (orientation) during processing, annealing, and the overall processing temperature can influence the molecular alignment and crystallinity, thereby impacting tensile strength. For example, biaxially oriented PLA films can achieve much higher tensile strengths than unoriented films.

Moisture Content: For hydrophilic bioplastics (like starch and chitosan), ambient humidity and moisture absorption can significantly plasticize the material, leading to a reduction in tensile strength.

8.1.4 Practical Implications for Applications

Packaging: For applications like flexible packaging, bags, or rigid containers, sufficient tensile strength is vital to prevent rupture, tearing, and damage during filling, sealing, transportation, and consumer handling.

Load-Bearing Applications: Higher tensile strength allows bioplastics to be considered for more demanding applications, such as durable consumer goods, agricultural films requiring tear resistance, or even some automotive components.

Durability: Adequate tensile strength contributes directly to the overall durability and longevity of a bioplastic product, impacting its useful life and functional performance.

The "Figure 1: Bar Chart showing the minimum and maximum values of tensile strengths (in MPa) for the three major types of bioplastics" would be a valuable visual aid alongside this improved discussion, as it directly supports the quantitative comparison.

8.2 Thermal Properties

In figure 2, glass transition temperatures (T_g) range between 55°C - 60°C for PLA and PHA, [67] while starch-based plastics display a glass transition temperature (T_g) of 57.2°C [68]. Meanwhile, chitosan has a T_g value between 118°C - 250°C [69]. The glass transition temperature being a quality that significantly impacts a material's strength, stiffness, flexibility, and resistance to cracking or deformation. It is the temperature at which a material transitions from a hard, glassy state to a more flexible, rubbery or viscous state. It is an important property used to change the physical properties of polymers. Increasing Tg improves handling characters, solubility, and reproducibility in the dissolution of solids.

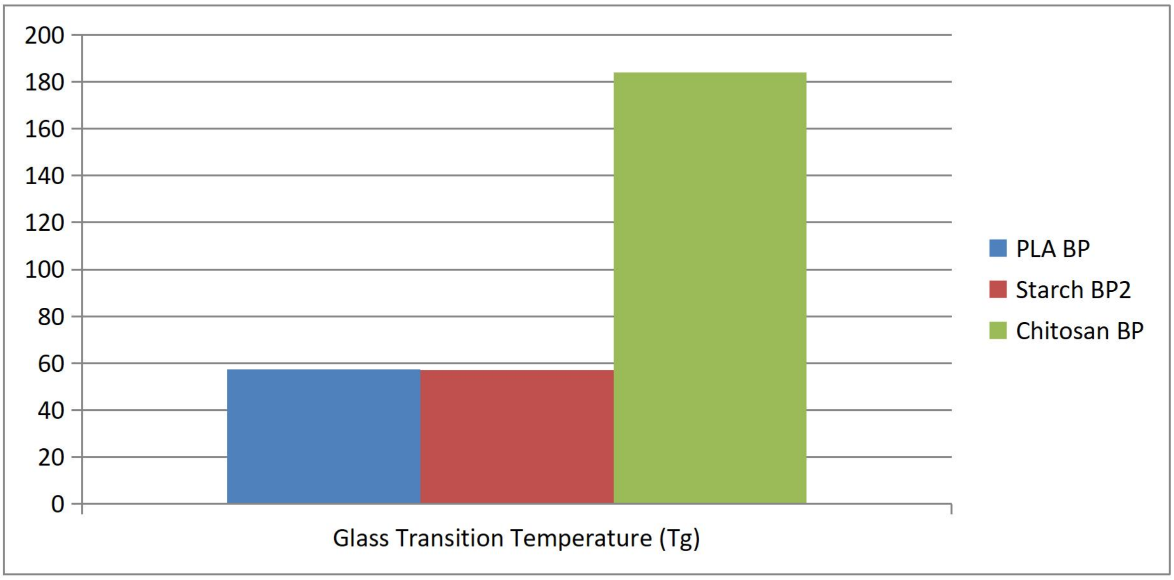

Figure 2. Glass Transition Temperature (Tg), for the three major bioplastic

8.2.1 Thermal Properties: Unpacking the Significance of Glass Transition Temperature (Tg)

The Glass Transition Temperature (Tg) is a fundamental thermal property that profoundly influences a polymer's mechanical behavior, including its strength, stiffness, flexibility, and resistance to cracking or deformation. It marks the reversible transition of an amorphous polymer or the amorphous regions within a semi-crystalline polymer from a rigid, brittle, "glassy" state to a more flexible, "rubbery" or viscous state as temperature increases. Beyond this point, the polymer chains gain significant molecular mobility, leading to a notable change in physical properties.

The provided Tg values for common bioplastics are:

PLA (Polylactic Acid) and PHA (Polyhydroxyalkanoates): Both exhibit Tg values ranging between 55°C and 60°C.

Starch-based plastics: Display a glass transition temperature (Tg) around 57.2°C.

Chitosan: Shows a significantly higher Tg value, typically ranging between 118°C and 250°C.

These reported Tg values highlight critical considerations for the application of these bioplastics:

8.2.2 PLA, PHA, and Starch-based plastics (Tg ~55-60°C)

Limited Heat Resistance: A Tg in this range means these materials will begin to soften and lose their structural integrity at relatively low temperatures, close to those encountered in hot tap water, hot beverages, or direct sunlight in warm climates.

Application Constraints: This makes them less suitable for applications requiring high heat resistance, such as packaging for hot-filled foods, microwaveable containers, or items exposed to elevated temperatures during transport or storage. For instance, a PLA cup might deform when filled with hot coffee.

Advantages for Certain Uses: However, this lower Tg can be advantageous for processing, allowing for easier thermoforming and molding at lower temperatures. It can also contribute to their potential for faster degradation in composting environments once the material softens and allows microbial access.

8.2.3 Chitosan (Tg ~118-250°C)

Superior Thermal Stability: Chitosan's significantly higher Tg indicates much greater thermal stability and rigidity at elevated temperatures compared to PLA, PHA, and starch-based plastics.

Broader Application Potential: This property makes chitosan a more suitable candidate for applications demanding higher heat resistance, such as some food packaging, biomedical devices that undergo sterilization, or structural components where thermal stability is crucial.

Processing Challenges: While beneficial for end-use properties, a higher Tg can sometimes make processing more challenging, potentially requiring higher temperatures or specific plasticizers to improve melt processability.

8.2.4 Comparison to Conventional Plastics

To put these values in perspective, it's useful to compare them to common conventional plastics:

Polyethylene (PE) and Polypropylene (PP): These typically have very low Tg values (e.g., LDPE ~-100°C to -120°C, HDPE ~-120°C, PP ~-10°C to -20°C). They remain flexible and usable over a wide temperature range, well below room temperature, making them excellent for flexible packaging and cold-storage applications.

Polyethylene Terephthalate (PET): Commonly used in beverage bottles, PET has a Tg of approximately 70-80°C. This allows PET bottles to handle ambient temperatures well but makes them unsuitable for hot-filling without specific heat-setting treatments.

Polystyrene (PS): Used for disposable cups and food containers, PS has a Tg around 100°C, providing good rigidity at room temperature but limiting its use in hot applications.

8.2.5 Factors Influencing Tg

The actual Tg of a bioplastic can be influenced by several factors:

Molecular Weight: Higher molecular weight generally leads to higher Tg due to increased chain entanglement.

Crystallinity: While Tg primarily relates to the amorphous regions, a higher degree of crystallinity can indirectly influence the mobility of the amorphous phase, potentially affecting Tg.

Plasticizers: The addition of plasticizers (e.g., glycerol, sorbitol in starch films) is a common strategy to lower Tg, thereby increasing flexibility and processability. However, this can sometimes come at the expense of mechanical strength and barrier properties.

Moisture Content: For hydrophilic bioplastics like starch and chitosan, moisture acts as a plasticizer, significantly lowering their effective Tg. This means that in humid conditions, these materials can become softer and more flexible than their dry Tg might suggest.

Additives and Fillers: The incorporation of reinforcing fillers or nanoparticles can restrict polymer chain mobility, potentially leading to an increase in Tg.

8.2.6 Importance of Tg for Material Properties

The glass transition temperature is a critical design parameter for bioplastic products because:

Mechanical Performance: Below Tg, the material is hard and brittle, while above Tg, it becomes softer, more rubbery, or viscous. Understanding Tg is essential to ensure the product maintains its structural integrity and desired mechanical properties under anticipated service temperatures.

Processing: Knowing the Tg is crucial for selecting appropriate processing temperatures (e.g., for extrusion, injection molding, or thermoforming) to ensure efficient shaping without degradation.

Product Stability and Shelf Life: For packaging, a Tg significantly above the expected storage and use temperatures is generally desired to prevent deformation or loss of barrier properties. For some applications like disposable cutlery, a Tg above typical food service temperatures is necessary to maintain stiffness.

The statement "Increasing Tg improves handling characters, solubility, and reproducibility in the dissolution of solids" in the original text likely refers to specific polymer processing contexts where a higher Tg might indicate better dimensional stability during handling of intermediate products or better control over the dissolution process for certain polymer forms, not necessarily for general end-use properties of finished bioplastic products like packaging films.

8.3 Water Vapour Permeability (WVP) in Bioplastics

Water Vapour Permeability (WVP) is a crucial property for bioplastics, particularly in packaging applications, as it dictates the material's ability to resist the passage of water vapor. This characteristic directly influences the shelf life of moisture-sensitive products, preventing issues like dehydration, spoilage, or textural changes [70].

The provided WVP values illustrate the considerable variation among different bioplastic materials:

PLA (Polylactic Acid) bioplastic: A WVP of 161.1 g mm/(m² day atm) is given.

Starch bioplastics: Showed a WVP of 0.001374 g m/(day m²). It is important to note that the unit for starch bioplastics (g m/day m²) is not directly comparable to the g mm/(m² day atm) unit used for PLA and chitosan, as it lacks a pressure component and the thickness unit is in meters rather than millimeters. This makes direct quantitative comparison difficult without further context on the measurement conditions or intended interpretation of the unit. However, starch-based films are generally known for their relatively high hydrophilicity and thus higher WVP, often requiring modification to improve their barrier properties [71].

Chitosan: WVP ranged from 3.34 to 4.7 g mm / (h m² KPa). To facilitate comparison with PLA, let's convert this range to g mm/(m² day atm):

Using the conversion factors: 1 atm = 101.325 KPa and 1 day = 24 hours.

Minimum WVP for Chitosan: 3.34 g mm/(h m2 KPa)×(24 h/1 day)×(101.325 KPa/1 atm)≈8125 g mm/(m2 day atm)

Maximum WVP for Chitosan: 4.7 g mm/(h m2 KPa)×(24 h/1 day)×(101.325 KPa/1 atm)≈11430 g mm/(m2 day atm)

Comparing the values, PLA (161.1 g mm/(m² day atm)) generally exhibits a significantly lower WVP than Chitosan (ranging from ~8125 to ~11430 g mm/(m² day atm)). This indicates that PLA, on its own, offers a considerably better barrier against water vapor compared to chitosan. While the starch value is problematic for direct comparison, it's widely understood that unmodified starch bioplastics typically possess high WVP due to their hydrophilic nature.

For context, many conventional plastics used in packaging, such as polyethylene (PE) and polypropylene (PP), exhibit extremely low WVP values, making them excellent moisture barriers. For instance, low-density polyethylene (LDPE) can have WVP values in the range of 0.5 to 1.5 g mm/(m² day atm), significantly lower than that of PLA.

8.3.1 Factors Influencing WVP

Several factors dictate the WVP of bioplastics:

Polymer Type and Chemical Structure: Hydrophilic polymers, rich in hydroxyl (-OH) groups (e.g., starch, chitosan, cellulose), tend to absorb more moisture and thus generally have higher WVP. More hydrophobic polymers (e.g., PLA, though less hydrophobic than PE) will inherently offer a better barrier.

Crystallinity and Molecular Packing: Higher degrees of crystallinity and more compact molecular packing within the polymer matrix create a more tortuous path for water vapor molecules, thereby reducing WVP.

Thickness: While WVP values are often reported as a material coefficient (normalized for thickness), for a given material, a thicker film will have a lower Water Vapor Transmission Rate (WVTR) - the actual amount of water vapor passing through per unit area over time.

Plasticizers: The addition of plasticizers (e.g., glycerol in starch films) can increase the free volume and chain mobility within the polymer, often leading to an increase in WVP.

Additives and Fillers: Incorporating hydrophobic additives (such as waxes like beeswax, essential oils, or lipids) or impermeable nanofillers (e.g., nanoclays, cellulose nanocrystals) can significantly enhance the barrier properties by increasing the path length for water vapor or by filling voids in the polymer matrix.

Relative Humidity (RH) Gradient: The driving force for water vapor permeation is the partial pressure difference of water vapor across the film. WVP can also be influenced by the surrounding humidity conditions, as some hydrophilic polymers exhibit increased permeability at higher relative humidities.

8.3.2 Impact on Applications

The WVP of a bioplastic is a critical determinant for its suitability in specific applications:

Low WVP Requirements: For products that are sensitive to moisture gain or loss (e.g., dry foods like biscuits, cereals, snacks, electronic components, pharmaceuticals), packaging materials with low WVP are essential to maintain quality and extend shelf life. Bioplastics often struggle to match the excellent moisture barrier properties of conventional polyolefins for these applications.

High WVP Requirements (Breathable Packaging): Conversely, some applications, particularly packaging for fresh produce like fruits and vegetables, may benefit from higher WVP. This "breathable" packaging allows for controlled respiration, prevents the accumulation of condensation, and helps maintain the freshness of the produce by allowing excess moisture to escape.

8.3.3 Strategies for Improvement

Researchers are actively developing strategies to improve the water vapor barrier properties of bioplastics to broaden their applicability. These include:

Blending: Combining hydrophilic biopolymers with more hydrophobic polymers (either other bioplastics or synthetic polymers like PBAT).

Surface Coatings and Multilayers: Applying thin barrier coatings or creating multi-layered structures with a low WVP layer.

Incorporation of Hydrophobic Additives: Adding natural waxes, lipids, or essential oils that are inherently water-repellent.

Nanocomposites: Dispersing impermeable nanoparticles (e.g., nanoclays, cellulose nanocrystals, graphene oxide) within the polymer matrix to create a more tortuous path for water vapor.

Chemical Modification and Cross-linking: Modifying the chemical structure of the biopolymer or cross-linking polymer chains to reduce hydrophilicity and enhance barrier properties.

8.4 Biodegradability of Agro-Waste Bioplastics

Agro-waste bioplastics offer a promising avenue for sustainable materials, with most exhibiting biodegradability under composting conditions. While the broad timeframe of 30 to 180 days for degradation is commonly cited, the actual rate is intricately influenced by a complex interplay of material properties and environmental factors.

8.4.1 Key Factors Influencing Degradation

Thickness: Thinner bioplastic materials generally present a larger surface area relative to their volume, allowing for more extensive microbial and enzymatic attack, thus accelerating degradation.

Crystallinity: The molecular arrangement within the bioplastic significantly impacts its degradation. Amorphous (disordered) regions are typically more accessible to water and enzymes, leading to faster degradation compared to highly crystalline (ordered) regions. For instance, amorphous polylactic acid (PLA) degrades more easily than its crystalline counterpart.

Environmental Factors in Composting: Composting environments provide a controlled setting optimized for biodegradation. Critical environmental parameters include:

Temperature: Higher temperatures, particularly those found in industrial composting (often peaking around 70°C and remaining above 50°C), significantly accelerate the hydrolysis of polymers and enhance microbial activity. Mesophilic (moderate temperature) and thermophilic (high temperature) phases in composting dictate the type and activity of microorganisms present.

Moisture Content/Humidity: Water is crucial for the hydrolytic degradation of polymers and for facilitating microbial growth and enzyme activity. Optimal moisture levels ensure that microorganisms can thrive and enzymes can effectively interact with the material.

pH: The pH level of the composting environment influences the activity of specific microorganisms and their enzymes. While compost pH can stabilize around 8.16, variations can impact degradation rates.

Oxygen Availability (Aerobic Conditions): Composting is primarily an aerobic process. The presence of sufficient oxygen is essential for the respiration of aerobic microorganisms, which are largely responsible for breaking down organic matter and converting carbon to carbon dioxide and water. Anaerobic conditions, such as those found in landfills, lead to much slower degradation and can produce methane.

Microbial Population and Enzyme Activity: The diversity and abundance of microorganisms (bacteria, fungi, archaea) and the specific enzymes they produce are paramount. Enzymes like N-acetyl-β-glucosaminidase, esterase, β-glucosidase, acid phosphatase, and alkaline phosphohydrolase play crucial roles in cleaving polymer chains into smaller molecules that can then be assimilated by the microbes. The presence of nitrogen-rich components in agro-waste bioplastics can also enhance microbial activity.

8.4.2 Mechanisms of Biodegradation

The biodegradation of bioplastics in a composting environment typically proceeds through three main stages:

Biodeterioration: This initial stage involves surface-level changes in the bioplastic's mechanical, physical, and chemical properties due to exposure to heat, moisture, and initial microbial colonization. This weakening of the material's structure facilitates further degradation.

Biofragmentation: In this lytic process, microorganisms, often aided by extracellular enzymes, cleave the polymer bonds, breaking down the long polymer chains into smaller oligomers and monomers.

Assimilation (Mineralization): The resulting oligomers and monomers are then absorbed and metabolized by the microorganisms as a source of carbon, energy, and nutrients, leading to the complete mineralization of the bioplastic into carbon dioxide, water, and new biomass. For a material to be certified compostable, typically over 90% of its carbon content must be converted to carbon dioxide within six months under controlled composting conditions (e.g., ASTM D5338).

8.4.3 Beyond Composting Conditions

It is crucial to note that the degradation rates observed in controlled industrial composting environments are significantly faster than those in less controlled settings like soil or home composting. Soil environments often have lower temperatures, variable moisture, and different microbial communities, which can lead to much slower degradation of bioplastics like PLA (e.g., taking many months or even years compared to weeks in industrial compost). The chemical structure and functional groups of the biopolymer, as well as the presence of additives or fillers, also influence how readily it can be degraded by microorganisms.

Most agro-waste bio-plastics degrade within 30-180 days under composting conditions, depending on thickness, crystallinity, and environmental factors [72].

9. Conclusion

Bio-plastics sourced from agro-wastes offer a sustainable, biodegradable, and environmentally friendly alternative to fossil-derived plastics. Their development leverages waste valorization, promoting circular economy principles. This meta-analysis shows a growing diversity of polymer types, production and synthesis methods, underscoring the feasibility of agro-waste as a valuable feedstock, with the resultant bioplastics indicating good qualities in terms of tensile strength, glass transition temperature, water vapour permeability, and biodegradability (with chitosan showing the highest range values while starch showed the lists). These properties also shows potential for improvement via modifications with additives.

For many reasons, bio-plastics, present a much better, environmentally friendly, economical and healthier substitute for conventional plastics. These include the biodegradability, source of raw material, lower carbon footprint and etc that the bio-plastics possess. Even though the first generation of bio-plastics were biomass dependent and the bio-based polymers were mainly comprised of polymers derived from agricultural feedstock and food products such as potato, corn and other carbohydrate sources, in more recent years, the focus has shifted because of the desire to move away from food based resources and because of significant breakthroughs in bio-technology now, there are more interests in agro-waste which is more preferable as it promotes recycling and avoids the problem of food scarcity.Hence more focus of research on it is paramount to improve this.

Also, rules should be put in place by governments around the world to ensure the application of bio-plastics; especially produced from agro-waste, in our everyday consumer products, especially products meant for one time use.

From the discussions done in this work, the advantage of bio-plastics cannot be overemphasized. It is and undeniable fact that plastics have some irreplaceable functions and roles, but even as we put them to use, it is necessary to put into consideration the fact that they are barely degradable. And even when they are, it takes thousands of years which leads to excess environmental pollution and degradation of health of our ecological system as it is obtained from report that every single plastic that was produced in the last century are still present here, and no means of them leaving anytime soon unless they are consciously artificially recycled. So also, laws should be put in place to ensure the proper recycling of plastics, both the already existing ones and those yet to be produced, as this is for both the conservation and health of our environment and planet.

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