A Biodegradable Poly(Vinyl Alcohol)/Hemp Fiber/Starch/Montmorillonite Composite for Sustainable Packaging

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INTRODUCTION

Since their invention at the beginning of the 20th century, plastics have brought many social and technological benefits. Lightweight parts for cars and aircraft greatly reduce fuel consumption and cut CO₂ emissions. High-performance insulation reduces home heating costs, and is also used in clothing to provide added warmth. Plastic packaging reduces food waste while also improving food safety. Countless medical innovations have been made using plastic tools, saving human lives.

Despite these successes, the way society produces, uses, and discards plastic has become a major environmental concern. 360 million tons of plastic are now produced each year, only 9% of which are recycled. By the year 2050, it is estimated that the mass of plastic in the oceans will exceed the mass of all fish species combined.¹ The majority of these plastic materials are neither renewable nor biodegradable, and can persist in the environment for centuries or even millennia.

For these reasons, consumers are increasingly demanding more sustainable options for plastic products. Plastics made from bio-based sources make up less than 1% of all plastics produced today, yet this market is expected to grow from 2.11 Mt/year (2019) to 2.42 Mt/year by 2024.² (Figure 1)

Figure 1: Current and forecasted global production capacity of bioplastics. Adapted from reference 2.

As plastics are so ubiquitous in society, rethinking the plastics value chain will require cooperation from producers, recyclers, consumers, waste management, and government. Continued innovation from the private sector will also be needed to drive growth and investment.

The term ‘bioplastics’ can refer to materials that are either bio-based, biodegradable, or both. This term can be confusing to consumers, as plastics can be made from bio-based feedstocks that are not biodegradable at all. Similarly, it is possible to produce fully biodegradable polymers from petrochemical feedstocks. The source of a plastic does not determine its biodegradability. Some example bioplastics are highlighted in Figure 2.

BIODEGRADABLE VS COMPOSTABLE

Biodegradation is the breakdown of organic matter by microorganisms such as bacteria and fungi. In the first stage of biodegradation, a material is broken down into smaller pieces by microbial action and weathering. Microbial enzymes then break down the material into smaller fragments that can be absorbed through microbial cell walls. Finally, the material is assimilated by the microbes and converted into biomass, as well as small molecules such as carbon dioxide (CO₂), methane (CH₄), nitrogen (N₂), ammonia (NH₃), and water (H₂O). Depending on the composition of the material, inorganic compounds like nitrates, silicates and phosphates may be produced as well.

Composting refers to accelerated biodegradation in a specific environment created by humans. Diverting organic waste from landfill to compost reduces greenhouse gas emissions, provides a source of fertilizer, and can also be a source of

Figure 2: Bio-based and biodegradable plastics.

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¹. Reference 1
². Reference 2
renewable natural gas. Compost can enrich soil with essential nutrients for growth, reduce erosion, and help control diseases in cropland. Composting also collects biodegradable materials in a centralized location and speeds up their decomposition, so they do not litter the environment as they break down. Composting technologies exist that can also break down organic matter that would not ordinarily biodegrade in the environment.

Composting facilities are examples of ‘managed environments’, where temperature, humidity, and aeration are controlled to varying degrees. Unfortunately, a significant amount of the waste generated by humans is simply discarded into the environment, where the conditions affecting biodegradation are not managed at all. (Figure 3) These ‘unmanaged environments’ include soil, seawater, and freshwater, and contain far fewer bacteria than active compost. For this reason, designing a biodegradable plastic that breaks down in these environments remains a major challenge.

Nearly 50% of compostable plastics sold today do not readily degrade in unmanaged environments, requiring specialized facilities to break them down. These include popular materials such as poly(lactic acid) (PLA), poly(butylene adipate terephthalate) (PBAT) and poly(butylene succinate) (PBS). While polyhydroxyalkanoates (PHAs) are an increasingly popular bioplastic that is degradable in soil and marine environments, the cost of these materials remains prohibitive for many applications.

BIODEGRADABLE PVA/HEMP COMPOSITES

To confront the global problem of plastic pollution, biodegradable plastics are urgently needed. Due to an explosion of recent research into compostable materials technology, it is now possible to design bioplastics that are cost-competitive with traditional petroleum-derived plastics while emulating many of their desirable properties. Such a material should be:

1. Biodegradable in both managed and unmanaged environments;
2. Degradable to only nontoxic byproducts;
3. Compatible with current technologies for plastics manufacturing;
4. Composed of recycled bio-based materials;
5. Cost-competitive with traditional plastics;
6. Similar in look and feel to a traditional plastic.

Here we describe a compostable formulation based on thermoplastic starch (TPS), polyvinyl alcohol (PVA), hemp fiber, clay, and glycerol designed to meet these criteria (Figure 3). A description of each of these ingredients, evidence for their biodegradability, and synergistic role in the formulation is described.

![Figure 3: Components of a versatile biodegradable plastic.](image)

**POLYVINYL ALCOHOL (PVA)**

PVA is a petroleum-derived water-soluble thermoplastic polymer with a backbone composed only of carbon atoms. Unlike most vinyl polymers, PVA is not produced from the polymerization of the corresponding vinyl monomer, due to the propensity for vinyl alcohol to tautomerize to acetaldehyde. Instead, it is produced from the hydrolysis of polyvinyl acetate (PVAc), which is commonly used in coatings and adhesives (most notably white glue). PVAc is typically produced by free radical polymerization from vinyl acetate in alcoholic solution (e.g. methanol or ethanol), though suspension polymerizations are also possible. The molecular weight of the parent PVAc polymer is normally determined by the monomer feed rate, initiator concentration, temperature, concentration, and residence time in the reactor.

The mechanical properties and water solubility of PVA are highly dependent on its degree of hydrolysis (DH). The DH indicates the percentage of PVAc units in the precursor material that have been converted to PVA, and typically ranges from 85-99.5%. PVA films with higher DH tend to have higher Young’s modulus, tensile...
strength, water vapour permeability, and elongation at break than films with lower DH.6

The properties of PVA make it useful across industrial, pharmaceutical, and packaging applications. It is odourless, has good optical clarity and thermal stability, and its mechanical properties can be readily tuned with additives. It is compatible with many techniques for plastics processing such as extrusion, injection molding, and blow molding. The deployment of these melt processing techniques is challenged by the proximity of its melting point and decomposition temperature, as PVA decomposition typically begins around 150 °C.

PVA decomposition can cause discoloration and the release of acetic acid (depending on the PVAc content), so care must be taken to avoid this. Fortunately, the addition of plasticizers such as water and glycerol can substantially increase the thermal stability and processability of the material. These improvements in industrial processing also enable effective recycling of the PVA scraps generated when manufacturing PVA parts. Chiellini et al. found no appreciable difference in molecular weight or dispersity of PVA samples recycled up to four times after melt processing.7

Global production of PVA now exceeds 1.2M tons/year. Polymers with all-carbon backbones such as polyethylene (PE), polypropylene (PP) and polystyrene (PS) are all non-biodegradable, but PVA is an unusual exception. Unlike these other examples, PVA is also water soluble. When a product containing PVA is submerged in water, it may break down or dissolve. Fortunately, water containing up to 5% PVA (50 g/L) has been shown to be nontoxic to fish,8 and the toxicity to humans when ingested is extremely low.9 Importantly, PVA films with DH < 90 % are completely soluble in water at 30 °C, while films with high DH (> 98%) require hot water (> 80 °C) to dissolve quickly and completely.

The biodegradation of PVA was first reported in 1936, when Nord reported the complete breakdown of PVA in the presence of Fusarium lini fungus.10 Several strains of microorganisms have been found which can efficiently use PVA as a source of carbon and energy.11,12 The most likely places to find these microorganisms are in soils nearby PVA factories,13 where they evolved specifically to consume this material. The difference in biodegradability is stark, with these acclimated microorganisms capable of consuming PVA at least 4 times faster than those in typical soils.13 While the breakdown of PVA can be slow if the right microorganisms are not present, it can be completely biodegraded if the right conditions exist.14 Indeed, microbial strains are now known which are capable of utilizing PVA as their sole carbon source.15,16

Biochemically, the breakdown of PVA is believed to be promoted by secondary alcohol oxidase (SAO) enzymes that are highly specific to PVA 1,3 diols.17 Studies have shown that single SAO proteins are able to produce a rapid drop in viscosity of PVA-containing solutions, suggesting a rapid reduction in molecular weight. Furthermore, the evolution of hydrogen peroxide during this process with consumption of O₂ is evidence of an oxidase mechanism.

Other studies have suggested a two-stage degradation mechanism, making use of β-diketone hydrolase (BDH) enzymes to efficiently break down PVA chains oxidized by SAO.18 These BDH proteins are highly specific to longer chain lengths, requiring at least five carbon atoms in the β-diketone structure to give efficient breakdown to lower molecular weight byproducts. (Figure 5)

More recently, microorganisms have been found that have evolved specific and highly efficient enzymes for PVA breakdown. Matsumura et al. discovered a specific PVA dehydrogenase (PVADH) enzyme which catalyzes the formation of β-hydroxyketone moieties along the PVA chain.19 These β-hydroxyketones are then broken down by an aldolase-type mechanism without further oxidation to β-diketones. Symbiotic bacterial strains capable of working together to break down PVA are also known.20

![Figure 5: Biodegradation of PVA by SAO and BDH enzymes.](image-url)
Though less well-studied, the breakdown of PVA by fungi and yeasts has also been described.\(^{21,22}\) In these studies, López and coworkers found that the LiP enzyme used by *Phanerochaete chrysoporium* fungi to break down lignin was also capable of degrading PVA. The authors suggested a mechanism that first proceeds through epoxidation, followed by the elimination of water to form C=C double bonds. Further investigations have revealed a diverse array of fungal species capable of PVA biodegradation, including *Saccharomyces*, *Lipomyces*, and *Rhodotorula* spp.\(^{23}\) Interestingly, the molecular weight and DH of a given PVA sample appear to have no effect on its extent of biodegradability.\(^{24}\)

The level of microbial acclimation to PVA is considered a critical parameter for the efficient biodegradation of PVA in soil or compost.\(^{25}\) Chiellini et al. carried out a detailed composting study on PVA under composting conditions approximating the ASTM D5338-92 standard.\(^{24}\) PVA blown films were placed in mature compost, with mesophilic (e.g. 28–37 °C), and thermophilic (e.g. 55–60 °C) temperatures applied. Biodegradation as measured by CO\(_2\) evolution reached only 7% in 48 days using non-acclimated compost. These results confirmed previous investigations by Bloembergen et al., which found that PVA degradation in compost reached 12% in 30 days.\(^{26}\) Similarly sluggish biodegradation of pure PVA samples has been reported in soils, achieving 8-9% breakdown in 74 days using respirometric tests. Though slow, these rates of breakdown are orders of magnitude larger than those of traditional plastics like PP, PE and PS.

Another factor that must be taken into account when explaining PVA’s slow degradation in non-acclimated environments is its strong binding to the mineral and organic components in soil. Solaro and coworkers attempted to quantify this effect by studying the rate of adsorption of PVA onto montmorillonite, quartz sand, farm soil, and humic acid. Soil itself is a complex mixture consisting of clays, silicates, organic compounds, and water, and by studying the interaction of PVA with these model substances, insight could be gained into the impact of PVA adsorption on its biodegradation.

Higher degrees of adsorption were observed for montmorillonite and farm soil, and the extent of adsorption was greater for PVA of lower molecular weight. Critically, the authors found that the extent of biodegradation was greatly reduced in liquid cultures of PVA containing montmorillonite compared to liquid cultures that did not (3% vs 34% after 27 days). This suggests that the adsorption of PVA onto clay particles in soil may partially explain its relatively slow rate of biodegradation. Furthermore, no detectable PVA was released when the montmorillonite samples were suspended in water, suggesting that this adsorption is very strong.

The impact of microbial acclimation on PVA biodegradation rates is similarly strong when considering aerobic biodegradation in aqueous environments. Remarkably, in the presence of sewage sludge from paper mill wastewater treatment plants, the rate of biodegradation of PVA is comparable to that of cellulose.\(^{24}\) This can be explained by the fact that local microbes face selective pressure from the large amount of PVA in paper mill wastewater. This kind of ‘directed evolution’ creates an environment where microorganisms that can use PVA as a carbon source will be more successful than those that cannot.

Indeed, Chiellini and coworkers have shown that it is possible to create microbial cultures specifically engineered for the biodegradation of PVA. By exposing cultures from paper mill sewage sludge to environments with PVA as the sole carbon source, bacteria could be engineered that broke down PVA significantly faster even than cellulose. In this case, >60% breakdown of PVA was observed in liquid cultures in as little as 28 days.

**THERMOPLASTIC STARCH (TPS)**

Starch is one of the most promising materials for the production of bio-based plastics due to its low cost, biodegradability, and readily renewable nature. Derived from foods such as corn, rice, wheat, potatoes and cassava, over 70 million tons of starch are produced annually. At present, the cost of starch per kilogram is below that of even common commodity plastics, making it an increasingly attractive material for large-scale manufacturing.

Starch itself is a mixture of the carbohydrates amyllose and amylopectin, each of which is a polymer of glucose. The ratio of linear amyllose to branched amylopectin varies by plant, with most containing 20-30% amyllose and 70-80% amylopectin.\(^{27}\) Films of pure starch are brittle, absorb moisture, and do not behave as thermoplastics (they cannot be melt processed), but these challenges can be overcome with the presence of suitable additives.
Figure 6: Chemical structures of amylose and amylopectin.

By blending starch with plasticizers such as water, glycerol, ethylene glycol, or sorbitol, it can be transformed from a brittle, powdery material into a thermoplastic. Starch is never used as a pure polymer in plastics manufacturing, but rather as a component of composites which may contain several ingredients. In this way, the tensile strength, elongation at break, Young’s modulus, glass transition, and gas barrier properties of TPS are highly tunable depending on the processing conditions and additives present. This versatility has made TPS suitable for broad applications including food packaging, flexible films, trays, straws, compost bags, and drug delivery capsules, among others.

For large-scale manufacturing, TPS pellets are normally produced by extrusion, by mixing the raw ingredients (starch, plasticizers, reinforcing agents) and chopping the extrudate into pellets. (Figure 7) These pellets may then be used in a secondary process such as injection molding, blow molding, or thermoforming to produce TPS plastic products. The global market for TPS is valued at approximately $500 million USD, and is expected to grow at a Compound Annual Growth Rate (CAGR) between 3.7-7% through 2025. Europe currently accounts for over half of TPS demand, a trend that is expected to continue due to incoming regulations banning single-use plastics.

TPS alone suffers from high water sensitivity and poor mechanical strength, but these issues can be overcome by blending starch with the right additives, such as plasticizers, natural fibers, nanoclay, or other biodegradable plastics. TPS composites can also be produced using starch from many botanical sources, including corn, wheat, cassava, rice, yams, peas, and others. In particular, low-cost starches rich in amylose, such as corn, potato or wheat are ideal, with moisture content between 10-20% by weight to yield optimal performance. Since starch is a nutrient for many different organisms and also one of humanity’s largest sources of food, it is readily biodegradable in unmanaged environments. Furthermore, TPS materials can also disintegrate in marine environments based on the solubility of starches in water, accelerating their degradation in lakes, rivers and oceans.

One drawback for the use of starch is that TPS products age with time, significantly changing the quality and shelf-life of the product. This is due to a process called retrogradation, in which the starch molecules in a plastic crystallize over time. Amylose and amylopectin molecules realign, packing tightly together into crystallites and pushing water and plasticizer out of the material. This increases tensile strength, decreases elongation, and decreases permeability to oxygen and water vapour. In other words, starch retrogradation makes TPS materials stiffer and more brittle. The botanical source of starch has a large effect on the rate of retrogradation, although there are no clear trends indicating why. The rate of retrogradation also increases greatly if the material is stored in a cool environment.

There are several ways to counteract the retrogradation of starch to increase the longevity of TPS materials. The addition of nanoclays such as montmorillonite to TPS significantly slows the rate of retrogradation to the point where starch crystallization is not observable over 90 days. This occurs because the clay particles bind strongly to the starch molecules, making it difficult for them to reorient into crystallites. PVA and glycerol monostearate also slow retrogradation, and in this way a bioplastic formulation can be designed to counteract this challenge as much as possible.

BLENDS OF PVA AND TPS

The addition of PVA is an effective way to improve the mechanical properties of a TPS material. Blends of TPS and PVA are highly compatible, and a mixture of the two in essentially any ratio will give a plastic material. By selecting a PVA feedstock with the right DH and viscosity, bioplastics with similar...
mechanical and tactile properties to common petroleum-derived plastics can be prepared. The biodegradability of starch/PVA blown films has been evaluated by recording the CO2 production and O2 consumption in a closed respirometer containing natural farm soil.\(^4\) After 82 days of incubation, samples containing pure potato starch as well as 10 and 20% PVA showed 82, 73, and 65% of CO\(_2\) evolution from the expected carbon content of the samples. This suggests that the rate of ultimate biodegradation of starch/PVA blends is negatively correlated with PVA content. From these data, it also appeared that the presence of the starch had no accelerating effect on the breakdown of PVA.

Detailed studies have also been carried out on Novamont’s Mater-Bi\(^\text{TM}\) films, which are composites of starch and PVA.\(^37\) These studies demonstrated convincingly that the presence of PVA-degrading \textit{Pseudomonas vesicularis} bacteria significantly increase the rate of biodegradation of these films.

Applying PVA-degrading enzyme was also particularly effective, greatly accelerating the rate of the material’s breakdown.\(^37\) This was attributed to the high activity of degrading enzyme at the beginning of the experiment, as well as the improved ability of the free enzyme to adhere to and permeate the material versus the bacteria themselves.

While the slow biodegradation of PVA in natural environments is typically attributed to the scarcity of PVA-digesting microorganisms, they may simply be present in lower numbers. Given a longer timeframe and the selective pressure of having PVA available as a carbon source, the right microorganisms will be more likely to achieve the population density needed to efficiently break down PVA.

HEMP FIBER

Polymeric materials have been reinforced with fillers to produce composites for nearly a century. Early biocomposites, like straw-mud construction materials, have existed since prehistoric times, with a similar purpose as those used today – to be low cost, lightweight, and strong. Incorporating natural fibers into a polymer matrix can strengthen the material by creating an interconnected, load-bearing fiber network. Biofiber composites are used in construction, automotive and aircraft parts, packaging, furniture, insulation, garden equipment, and toys. They can be processed using common techniques like extrusion, injection molding and 3D printing, among others.

Most biofibers are composed of cellulose, hemicellulose and lignin. Together, these three substances comprise ‘lignocellulosic biomass,’ the most abundant bioresource on earth, making up the majority of the dry mass of most plants. Bast fibers, like hemp, flax, kenaf, jute and ramie are used when composites with high strength and stiffness are required, and can be used in chopped, nonwoven or mat forms. (Figure 8)

Cellulosic fibers can enhance the gas barrier properties, water resistance, and thermal stability of TPS.\(^38,39\) Wood fibers and those from other sources have been extensively used in biocomposites due to their safety, biodegradability, and low cost. In the case of TPS, the improvements in mechanical properties are attributed to the strong binding between the fibers and the starch matrix, resulting in good stress transfer from the plastic to the fibers.

The reinforcement of commodity plastics with glass fibers (or carbon fibers) is also very common, and is used across applications from sporting equipment, vehicle parts, insulation, and windows. Natural fibers can achieve a similar goal in a more sustainable way, with approximately 1/3 the cost of synthetic fibers and 1/2 the weight.\(^40\)

![Hemp fibers](image_url)

**Figure 8**: Hemp fibers.

The advantages of using natural fibers in composites are their availability, low cost, low density, light weight, attractive mechanical properties, low thermal expansion, non-abrasiveness, and biodegradability. Disadvantages include their tendency to absorb water, their instability at high temperatures, and their susceptibility to microbial attack. By combining with other ingredients and optimizing processing temperatures, the effects of these drawbacks can be limited to unlock the potential of natural fiber composites.

Hemp fibers are among the most well-understood natural fibers, behaving similarly to glass fibers in terms of strength and stiffness. Hemp’s shape, colour, feel, and vibration-damping capacity\(^41\) give it a wide range of functionality and commercial uses. Furthermore, hemp fiber is very often treated as a
waste material, and can thus be incorporated into bioplastics at very low cost. Hemp compares favourably with other common sources of biofiber, and has been shown to provide greater reinforcement than bamboo, banana, ramie, cotton, and jute. As hemp fibers are a naturally occurring plant-based material, they are fully biodegradable in both managed and unmanaged environments.

Hemp fibers are well-known to improve the mechanical properties of TPS and PVA materials. In general, as more hemp is added to a TPS composite, the material will become harder and stiffer. Ochi prepared starch/hemp composites with up to 70% hemp fibers by volume. The author found a remarkable increase in tensile strength upon increasing the hemp content from 30–70%, more than doubling from 219 to 495 MPa. Similar increases were observed in flexural strength and elastic modulus, with both increasing linearly with increasing hemp content. Notably, the tensile strength of the composite decreased when the material was processed at temperatures above 180 °C but maintained its integrity after heating at 160 °C. These results indicated that composites containing hemp fibers should be processed at or below 160 °C to prevent thermal degradation.

These results are in agreement with those of Vilaseca and coworkers, who found that reinforcement with 20 wt% hemp fibers resulted in an 18-fold increase in Young's modulus and a threefold increase in tensile strength when compared to TPS containing no hemp. The authors also observed a significant reduction in the elongation at break from 20 ± 6% to 3.4 ± 1.1 upon the addition of 20% hemp, indicative of the increased stiffness of the resulting material. Furthermore, the use of hemp fibers was found to provide superior mechanical properties to TPS reinforced with sisal, attributed to better fibrillation of the hemp strands.

As plant fibers come from the tissues of a living organism, they are made of many substances beyond just those required for reinforcement. Hemp fiber consists of 73-77% cellulose, 7-9% hemicellulose, 4-6% lignin, pectin, and water, along with many other compounds. Cellulose is the main component attributed to the reinforcing ability of natural fibers in plastics.

Numerous studies have shown that composites containing plant fibers are improved when the fibers are pretreated with an alkaline (basic) wash. Stirring the fibers in a solution of sodium hydroxide in water removes the hemicellulose, lignin, and other impurities, greatly improving the ability of the fibers to bind to the TPS matrix. These treated fibers improve the ultimate strength and elongation at break of TPS composites by ~10% relative to untreated fibers, and are also less likely to detach from the plastic.

Alkaline treatment is the most widely used method for treating biofibers because it is both effective and cost-efficient. The process makes fibers both shorter and thinner, improving their adhesion to the resin. If the treatment is too aggressive however, it can degrade the fibers to the point that they do not act as effective reinforcement. This can occur if the fibers are stirred for too long, or if the sodium hydroxide concentration is too high.

NANOCLAY

Nanoclay is an environmentally friendly, naturally abundant, and low-cost filler for TPS materials. Just a few percent of clay can greatly improve the mechanical, thermal, and barrier properties of these materials, as well as reduce water absorption. The clay particles bind starch molecules tightly together, giving the product a longer shelf life. Composites of nanoclay, starch and PVA are also well-known to give biodegradable plastics.

Nanoclays are nanoscale particles of layered silicate minerals which have extremely high surface areas - a single gram of nanoclay can have a surface area of 600–800 m². Put differently, 7 grams of nanoclay has approximately the same surface area as an American football field, made possible due to the extremely small size of the clay particles. This high surface area allows a small amount of nanoclay to interact strongly with the surrounding material, dramatically changing its mechanical properties. Furthermore, nanoclays are made from naturally occurring minerals and are both readily available and inexpensive. While the individual clay particles are very small, the bulk material is sold as a simple powder. (Figure 9) Nanoclays make up 50% of all nanofillers used in polymer composites today.

Nanoclay can be added to TPS to improve its mechanical properties, water resistance, and thermal stability. The enormous surface area of nanoclays gives them a large number of interactions between the clay particles and the starch polymer, producing substantial changes in properties at relatively low loadings of nanoclay (<10 wt.%).
Nanoclays are used in TPS composites alongside plasticizers to give durable, moldable materials. The most common nanoclays include montmorillonite (MMT), perlite, sepiolite, and kaolinite, with each differing slightly in chemical formula. Of the many available types of clay particles, MMT is the most commonly used. MMT is inexpensive, readily available, and has chemical properties that are easy to control.\textsuperscript{51} TPS/nanoclay composites have been reported to have improved tensile strength, gas barrier, and thermal stability compared to TPS alone.\textsuperscript{52–54} Studies have also shown that nanoclay can greatly increase the strength of TPS plastics, as well as their barrier to water vapour.\textsuperscript{29,55}

As the popularity of nanofillers in consumer packaging continues to grow, interest in their safety and environmental impact has gained momentum. The migration of nanofillers into foods or other packaged goods has been shown to be very low as long as the particles are embedded in the plastic.\textsuperscript{50} In the US, bentonite and kaolinite nanofillers have been recognized as safe.\textsuperscript{56} They are also safe upon breakdown in the soil in compostable products – in fact, spreading nanoclay in sandy soils or deserts has recently been shown to dramatically improve water retention, allowing plants and crops to more easily grow.

**GLYCEROL AND GLYCEROL MONOSTEARATE**

Plasticizers are small, nonvolatile molecules that change the thermal and mechanical properties of polymers when added to them. Without plasticizers, starch is not a thermoplastic, but can readily melt and flow at high temperatures when the right plasticizers are added. Plasticizers disrupt the interactions between the starch polymer chains, increasing its ductility and lowering the melting point of the starch to below its decomposition temperature (230 °C) so it can be processed. The most common plasticizers for TPS are water, glycerol, ethylene glycol, sorbitol, sucrose, fructose, glucose, and urea.\textsuperscript{57,58}

Glycerol in particular is found in plant and animal sources in nature, particularly in triglycerides. It is water soluble, nontoxic, and widely used in the food industry as a sweetener and preservative. It is also used in the pharmaceutical and personal care industries in products such as cough syrups, toothpaste, skincare products, and hand sanitizer. Due to its excellent compatibility with starch and its safety in the environment, glycerol is an ideal plasticizer.

Naturally occurring glycerol derivatives can also be added to starch-based plastics to fine-tune their mechanical properties. Glycerol monostearate (GMS) is one such additive that has been shown to improve the properties of TPS. GMS is produced from plant and animal fats, and is also produced in the body from normal metabolism. Chemically, it is simply one molecule of stearic acid (a natural fatty acid) and one molecule of glycerol bonded together through a condensation reaction. It is used as a thickening and emulsifying agent in foods, as well as in cosmetic and hair care products.

GMS can substantially improve the processability of TPS.\textsuperscript{59} A small percentage of GMS can greatly reduce the melt viscosity of TPS, making the material flow much more easily as well as consume less energy during processing.

**SUMMARY AND FUTURE WORK**

Reversing the world’s addiction to non-biodegradable plastic is an urgent environmental challenge. While composting will be a critical part of shaping a sustainable future, the volume of plastic discarded into soils, lakes, rivers, and oceans demands a more universal solution. We believe that plastics capable of breaking down in unmanaged environments are the key to tackling the problem of global plastic pollution.

Here we have described a biodegradable plastic made from starch, PVA, hemp fiber, nanoclay, glycerol and GMS. (Figure 10) These ingredients act synergistically to give a hard material with the look and feel of conventional plastics that can be shaped into solid plastic or molded into films. Each of these ingredients breaks down to nontoxic byproducts after biodegradation. Furthermore, the properties of the final material are tunable with changes in the formulation, which will allow for the fine-tuning of the elastic modulus, ultimate strength, and elongation-at-break of materials in this family. Rates of biodegradation and hydrodegradation will also be tunable by changing the material’s composition. Importantly, these materials should be compatible with existing infrastructure for traditional plastics manufacturing, allowing for facile...
integration into established supply chains. We also anticipate that costs will be competitive with conventional plastics, driven by the very low cost of starch and hemp feedstocks.

Potential applications of these materials are wide-ranging given the diversity of mechanical properties available by tuning the formulation. The manufacture of high-volume products such as bioplastic cutlery and utensils is envisioned, and should be possible using techniques such as injection or compression molding. The manufacture of larger, hollow objects by rotational molding should also be possible, unlocking applications in double-walled containers with high strength and stability. Film fabrication using TPS/PVA composites is also well-established, using techniques such as extrusion blow molding. This will allow for the manufacture of single-use items such as films, bags, air pillows, bubble wrap, and mailers using a biodegradable material. With the addition of foaming agents, we anticipate that the manufacture of expanded hemp/PVA foams will be possible for applications in food containers and packing material such as ‘packing peanuts’. Finally, using injection molding and/or thermoforming, packaging for cosmetics, pharmaceuticals, and consumer goods will be broadly enabled.

Future work will include the comprehensive evaluation of the mechanical properties, compostability, and biodegradability of this new class of materials, as well as defining protocols and processes for its manufacture. Biodegradation in managed environments such as windrow composting, in-vessel composting, and anaerobic digestion will be investigated. Finally, we will also investigate the biodegradation of these resins in unmanaged environments such as soil, fresh water, and marine water.

![Figure 10: Bioplastic prototypes developed by CTK Bio Canada.](image)

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REFERENCES


