

## BIODEGRADABLE PLASTICS FROM CASSAVA STARCH IN THAILAND

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### ABSTRACT

The paper reviews the role of starch and biodegradable plastics production in Thailand, emphasizing the potential contribution of cassava starch in these products. Types of biodegradable plastics and their manufacturing processes are described. The major types of biodegradable plastics discussed are directly-expanded starch products and various starch-polymer blends (PCL, PLA, PVA and PHA). Research focusing on cassava starch incorporation into biodegradable plastics is summarized.

### INTRODUCTION

The world production of plastic is estimated to be more than 100 million tonnes per year. The need for such large quantities of conventional plastics and their dominance over other materials is due to their excellent “long-life” properties. These properties include resistance to chemical reactions, specially enzymatic reactions. For example, it can take up to one hundred years to degrade only a few grams of plastic (such as polyethylene) under normal environmental conditions. Degradation at high temperature, such as in pyrolysis (burning) tends to cause emission of toxic fumes. Plastic accumulation in the environment thus creates tremendous problems for the world, presently and in the future. Environmental problems caused by plastics include changes to the carbon dioxide cycle, problems in composting, and increased toxic emissions. Stimulated by environmental concerns, scientists are now concentrating on ways to develop plastic use more efficiently. Two simple strategies are to “recycle” (reuse), or to produce plastics that will degrade when no longer required.

Degradable plastics are grouped by the American Society for Testing and Materials (ASTM D20.96) as:

- a) Photodegradable plastics – A degradable plastic in which the degradation results from the action of natural daylight;
- b) Oxidatively degradable plastics – A degradable plastic in which the degradation results from oxidation;
- c) Hydrolytically degradable plastics – A degradable plastic in which the degradation results from hydrolysis; and
- d) Biodegradable plastics – A degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae.

As the plastics defined in categories a), b) and c) require additional inputs, such as light (UV) or oxygen for degradation, the biodegradable plastics (d) offer the only products which are “naturally” degradable.

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Biodegradable plastics are polymers or polymer blends, which in addition to possessing properties similar to conventional plastics are susceptible to “natural” enzyme hydrolysis or other chemical attack. The plastic is therefore either broken down to oligosaccharides or monomers, through “depolymerization”, or are degraded to gaseous components through mineralization. Starch, a natural polymer, is biodegradable and as such can play an important role in the biodegradable plastic manufacturing process. It is also inexpensive and renewable. In tropical countries cassava starch offers opportunities due to its purity, clearness of its paste and low cost of production. This starch also possesses properties that enable it to be blended with other expensive polymers required for producing biodegradable plastic. Projections for the requirement of biodegradable plastic, by the year 2000, is 1.68 million tonnes (**Table 1**).

**Table 1. Projections of world consumption of biodegradable plastics in the year 2000.**

Application	Quantity (million tonnes)
Trash bags	1.00
Agricultural	0.09
Food containers/utensils	0.18
One-way packaging	0.27
Food packaging	0.14
Total	1.68

*Source: Chemical Week, October 27, 1993.*

The “Cradle–To–Grave” concept (**Figure 1**) has been designed by the Michigan Biotechnology Institute (1994). As the end use of products from biodegradable plastic is composting, it can serve as a reserve for carbon dioxide and as a means to return nutrients back to the soil (as compost).

## MANUFACTURING PROCESS TECHNOLOGY

### 1. Starch Puff

This kind of product is known also as “Gelatinized starch puff” or “Plate expanded by extrusion” or “Baking with water”. The products are formed by the swelling and expansion of starch through the action of high temperature and water vapor. The products formed in the extruder are starch foam, snack, etc (**Figures 2 and 3**). Plate expansion or baking give products such as waffles, which can be formed in tray shapes or other packaging material.

Clean Green Company in Minneapolis, MN, USA, has produced “starch foam” called “peanut” (American name of loose fill packing material) by extrusion of wheat starch (90 portion) and polyvinyl alcohol (10 portion). “Eco–Foam”, a product of National Starch, uses waxy corn as raw material. In European countries, the baking technology is also at a commercial scale. Packaging products, such as fast food utensils, are available in the market using both cereal and potato starches. The marketing of biodegradable packaging products are supported in the EU.

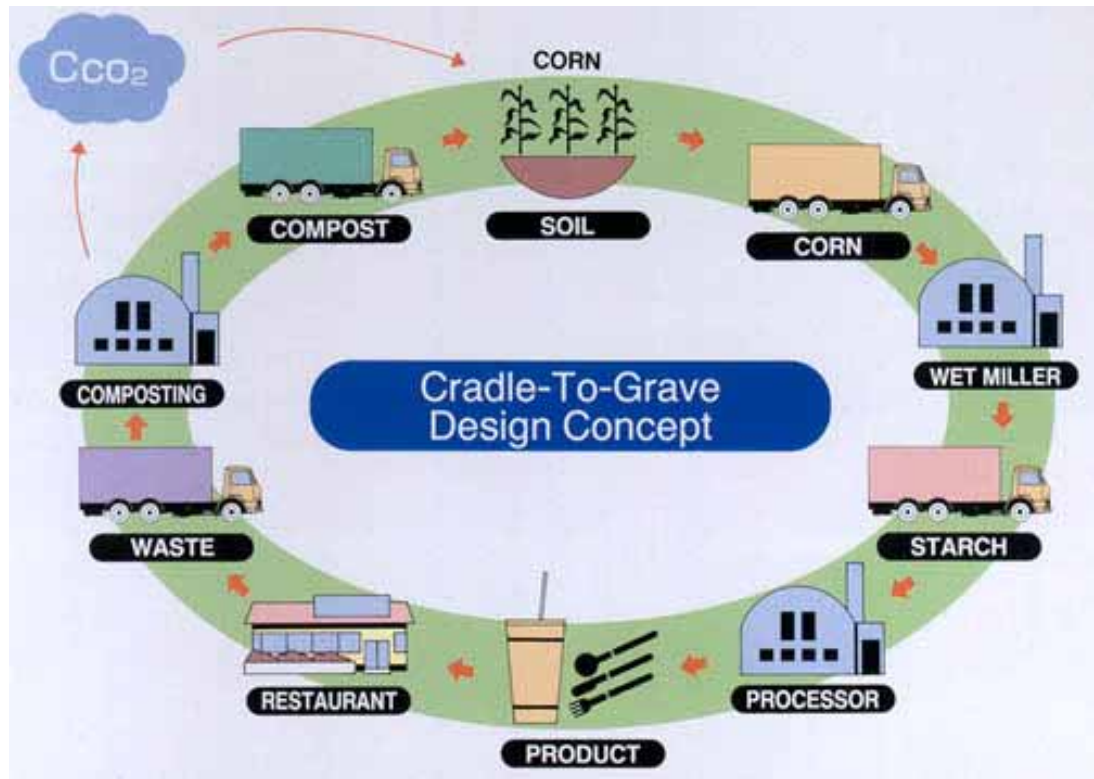


Figure 1. Design concept of biodegradable plastic “from cradle to grave”.  
 Source: Michigan Biotechnology Institute, 1994.

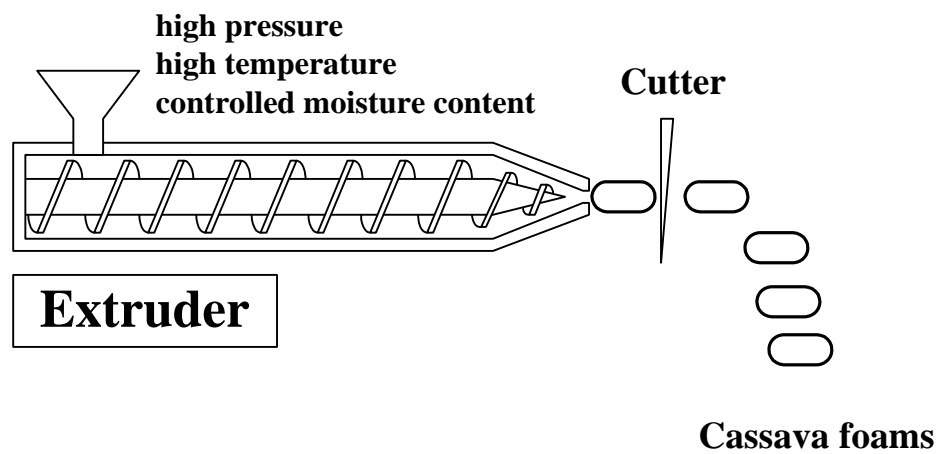
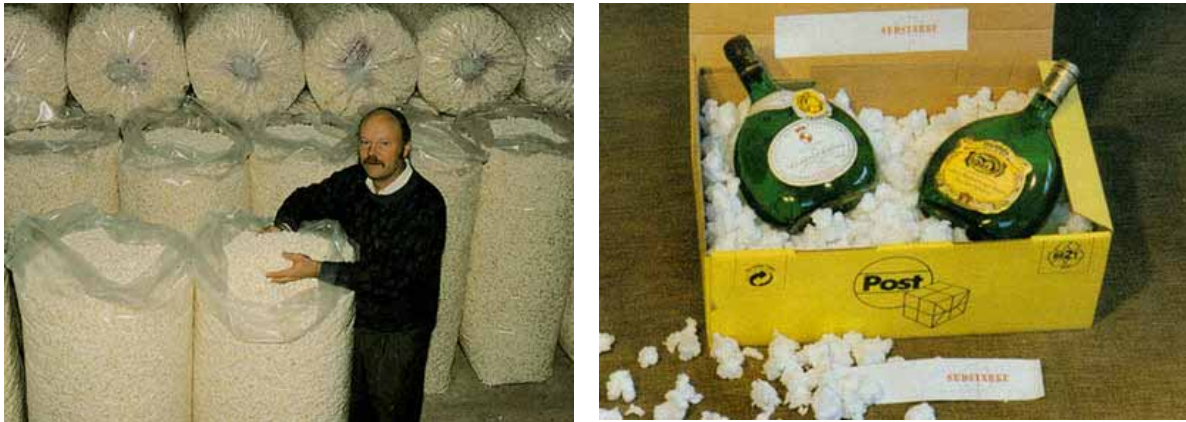


Figure 2. Extrusion of starch foam.



(a)

(b)

Figure 3. Starch foam: (a) Pesika Naturpack GmbH; (b) Suedstraerke GmbH.

Cassava starch has been successfully expanded under extrusion conditions. Due to its low bulk density, a little modification is needed so that its moisture content is increased. Twin screw extrusion is recommended for direct expansion of cassava starches. Cassava starch can also be used as the raw material for plate expanded or baking products. Cassava starch can be expanded in moulds, at 200-240°C for 1-3 minutes, to form into package utensils, such as bowls. About 10% additives, including calcium carbonate, agar, or emulsifier are needed to improve the properties. The bulk density is reported in the range of 0.15 to 0.176 g/cm<sup>3</sup> (Poovarodom and Praditduang, 1999)

Even though this group of products has been introduced to the market for some time, and can be produced at reasonable cost, constraints to its wider adoption still exist. First, special machinery is required, such as high shear extruder (not plastic extruder), continuous molding machine with high temperature (continuous waffle moulds using high pressure and temperature). Thus, the investment cost for the machinery is high. Distribution of the products is limited, due to its rigidity and short shelf life. Further, these products can not be applied to high moisture conditions. Lamination with other polymers, to improve shelf life and tolerance to high moisture conditions, will increase production cost, and such polymers have to be approved before using as a food packaging material.

## 2. Polymer/Starch Blends

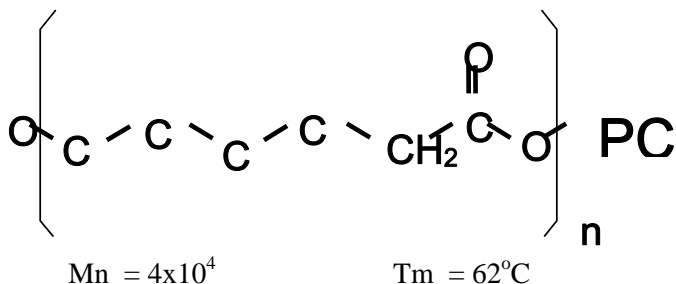
The biodegradable polymers (polylactic acid, polyhydroxyl butyrate) are in this group produced by fermentation (using starch hydrolysis products: glucose, maltose, etc.). The blending of polymers with starch under controlled conditions leads to copolymerization that in turn results in high molecular polymers with thermoplastic properties. Though the mixing or blending needs special machinery, such as an extruder, the products (polymer blend) can be handled as easily as conventional plastic resin.

Polymer blends can be distributed or transported to normal plastic converters, which can process the blends to products using normal injection or blow moulds.

## 2.1 Polymers

Though starch, such as that of cassava, is used as a polymer, other polymers are frequently used in the blend:

### a. Polycaprolactone

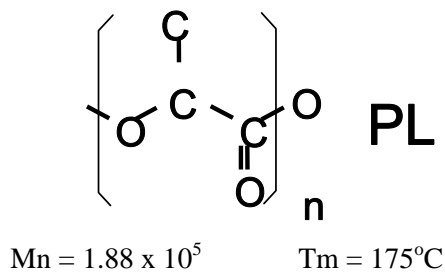


This polyester is manufactured by catalytic ring-opening polymerization of  $\epsilon$ -caprolactone. Union Carbide is the biggest manufacturer (**Table 2**). Polycaprolactone blend is the most used polymer/starch blend because of its low melting temperature ( $T_m$ ) and high susceptibility to amylase and lipase hydrolyses (Tokiwa *et al.*, 1990a; 1990b). A number of patents of polycaprolactone/starch blend are held:

- Michigan Biotechnology International (MBI), USA (US 5,578,691 etc.)
- Chuo Kajuku Co., Ltd, Japan (US 5,256,711 etc)
- Bioplastics Inc., Suite, MI.
- Daicel Chemical Industries Co., Ltd, Japan
- Japan Corn Starch, Japan

Most patents describe a generic starch, this includes cassava.

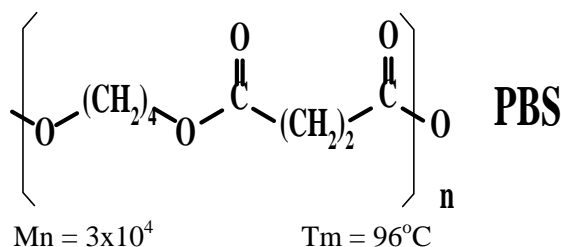
### b. Polylactic acid



This polyester is manufactured by catalytic ring-opening polymerization of lactide (dilactone of lactic acid). Cargill, Minneapolis, MN, USA is the biggest manufacturer (**Table 2**). Polylactic acid is used because lactic acid can be produced by microorganisms

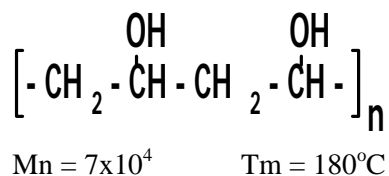
through a fermentation process. Many research laboratories in Japan claim that polylactic acid can be produced from a condensation-polymerization reaction of free lactic acid (from fermentation of starch). Polylactic acid from direct condensation polymerization is on the market under the names of “Lacty” (Shimadzu Corp. Japan) and “Lacea” (Mitsui Chemicals, Japan). These products offers the opportunity for a polymer blend totally derived from starch-based materials.

- Polybutylene succinate (PBS), and
- Polybutylene succinate/adipate (PBSA)



These products are derived from polycondensation of linear dicarboxylic acid with glycols. In the market they are sold under the name of “Bionolle” (Showa Highpolymer Inc., Japan); a wide range of molecular weights and properties are available.

*c. Polyvinyl alcohol (PVA)*



This is one of the most common synthetic polymers which can be easily biodegraded (Sakai *et al.*, 1987). However due to its solubility, applications are limited.

*d. Polyhydroxyalkanoates (PHA)*

This group of products are obtained from microorganisms through a fermentation process. Properties can be thermoplastic to elastomeric depending on the monomers used. The most popular product of this group is poly (3-hydroxybutyrate) (PHV).

The manufacturers and prices of polymers are shown in **Table 2**.

**Table 2. Manufacturers, capacity and cost of biodegradable polymers.**

Company	Base Polymer	Feedstock	Cost ( \$/lb)	Capacity (10 <sup>6</sup> million lb/yr)
Cargill, Minneapolis, MN	Poly lactide (PLA)	Renewable resources, Maize	1.00-3.00	10('94 scale up) ;250(mid-1996)
Ecochem, Wilmington, DE	Poly lactide Copolymers	Renewable resources, Cheese whey, Maize	<2.00 proj'd	0.15 ('94 scale up)
Zeneca (business unit of ICI)	Poly(hydroxybutyrate-co-hydroxyvalerate), PHBV	Renewable resources, Carbohydrates (glucose), organic acids	8.00-10.00; 4.00 proj'd	0.66, additional capacity slated for '96 is 11-22
Novamont, Montedison, Italy	Starch-synthetic polymer blend containing approx. 60% starch	Renewable resources Petrochemical	1.60-2.50	50, in Turni, Italy
Novon Products (Warner-Lambert), Morris Plains, NJ	Thermoplastic starch polymer compounded with 5-25% additives	Renewable resources, Starch	2.00-3.00	100
Union Carbide, Danbury, CT	Polycarpolactone (Tone polymer)	Petrochemical	2.70	<10
Air Products & Chemicals, Allentown, PA	Polyvinyl alcohol (PVOH) & Thermoplastic PVOH alloys (VINEX)	Petrochemical	1.0-1.25 (PVOH); 2.50-3.00(VINEX)	150-200 (water sol, PVOH); 5(VINEX)
National Starch & Chemicals, Bridgewater, NJ	Low DS starch ester	Renewable resources, Starch	2.00-3.00	Not available
MI Biotech Inst./GRT-Japan Corn Starch Joint Venture, MI	Water repellent, thermoplastic modified starches	Renewable resources, Starch	1.0-1.50	0.1 (pilot scale); 150 slated for early '96
Showa Highpolymer Co.,Ltd.	Condensation polymer of glycols with aliphatic dicarboxylic acids (BIONELLE)	Petrochemical	approx. 3.00	0.2 (pilot);7 (semi-commercial, end '94)
Shimadzu Corp. Technology Research Lab.	Poly (lactic acid) (Lacty)			Not available
Mitsui Chemicals, Inc.	Poly (lactic acid) (Lacea)			Not available

*Source: Narayan, 1994.*

## 2.2 Blending techniques

There are four ways to blend starch with polymer:

### a. Starch in the granular form

Mixing or blending starch with limited moisture content causes less loss of structure of the starch granule. Cassava starch can be completely gelatinized at 65-70°C with 45% moisture content, but the granule is maintained at a moisture content under 5%. The melting point ( $T_m$ ) of dry cassava starch (almost anhydrous) is about 170°C. After blending polymers with granular starch, the structure consists of a continuous polymer phase with starch granules embedded and reinforcing the network. This increases the strength, water absorption and vapor permeability, and decreases the production cost (**Figure 4**).

### b. Gelatinized starch

By controlling the moisture content, starch granule structure can be totally gelatinized at the same melting temperature as the polymer; thus, the two are blended together. This affords improved properties of elongation and tensile strength to the polymer (**Figure 4**).

### c. Thermoplastic starch

Under severe extrusion conditions, low moisture content, high temperature and pressure, starch can be melted. This thermoplastic starch is then a single component continuous phase. Thermoplastic starch was patented by Werner-Pfleiderer Co., Ltd, Germany.

### d. Modified starch

Modification of starch, such as addition of ester groups, to manipulate its properties supports the blending mechanism.

The manufacturing process is shown in **Figures 5 and 6**

Cassava starch blended with polycaprolactone (PCL) was developed in 1996 (Pranamuda *et al.*, 1996). Blended in the proportion of 50/50, the product exhibited a tensile strength of  $3.9 \pm 0.4$  MPa and % elongation of  $240.9 \pm 56.7$ . The effect of varying the proportion of cassava starch to PCL has also been investigated (Chollakup *et al.*, 1998). The tensile strength and % elongation of these products are shown in **Table 3**. Other attempts to improve final product quality, such as irradiation treatment (Chollakup *et al.*, 1999a, **Table 4**), inclusion of silk protein to the blend (Chollakup *et al.*, 1999b, **Figure 7**) and addition of sucrose ester (SE) as plasticizer (Sriroth *et al.*, 1999; **Table 5**) have been reported.

The Cassava and Starch Technology Research Unit, a research unit supported by the National Center for Genetic Engineering and Biotechnology (BIOTEC), the Thai Tapioca Development Institute (TTDI), and Kasetsart University (KU), conducts research on modification of cassava starch for blending with polymers.



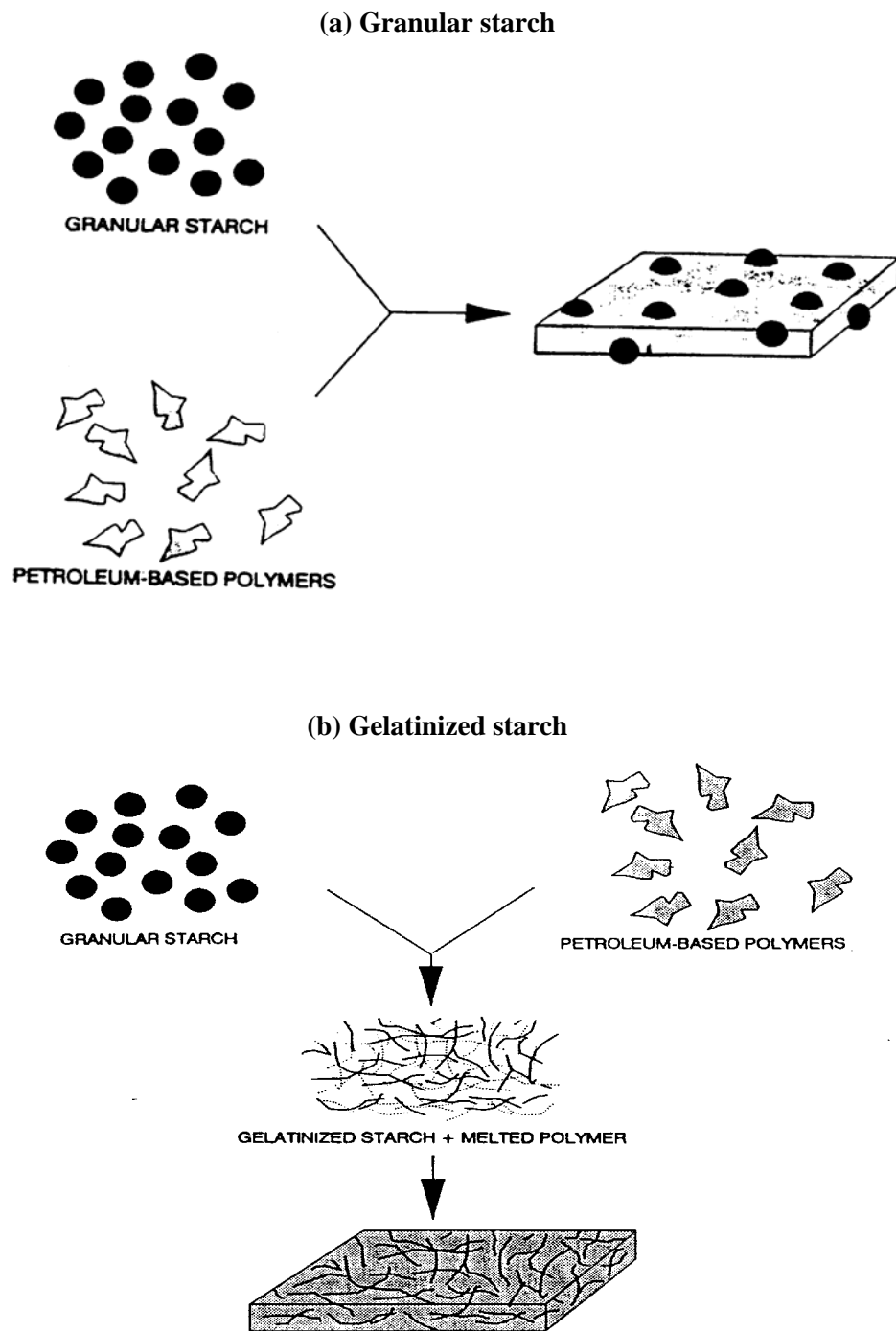


Figure 4. Characteristic of granular and gelatinized starch as blending material for polymer blend.

Source: Gould et al., 1990.

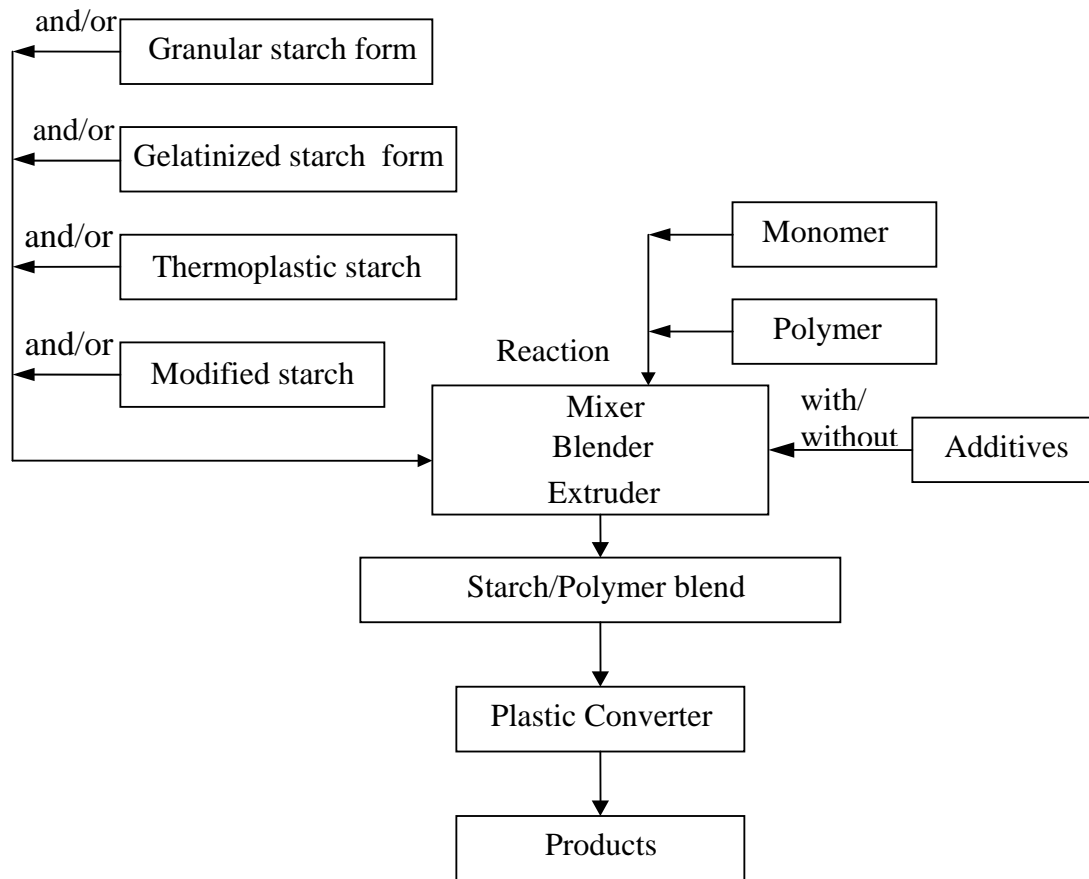


Figure 5. Biodegradable starch plastic manufacturing process.



Starch/Water/Polymer  
or Plasticizer

Blend in  
single screw extruder

Molding by  
heat press machine

Testing mechanical properties and biodegradability

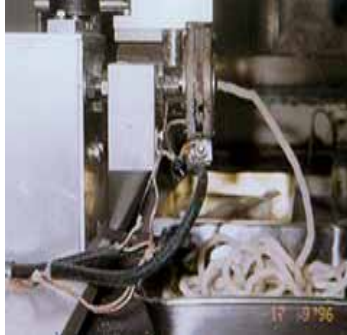


Figure 6. Extrusion process of biodegradable plastic.

**Table 3. Physical properties of cassava starch/PCL blends using granular (TS) and gelatinized (GS) starch in various proportions.**

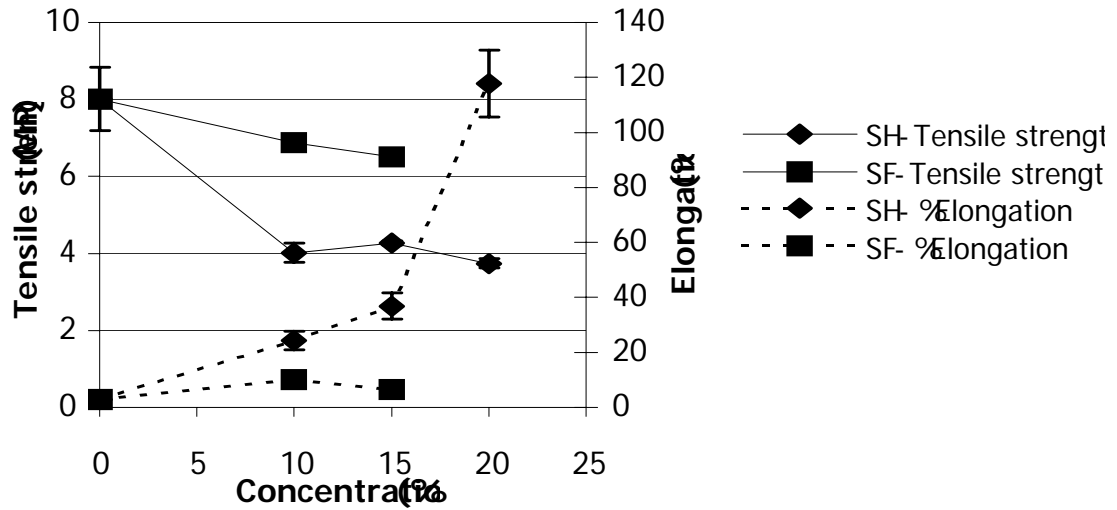
	Tensile strength (MPa)	Elongation (%)
<b>Granular starch (TS)</b>		
TS/PCL (0/100)	30.40 ± 4.6	613.40 ± 108.5
TS/PCL (10/90)	19.40 ± 3.4	435.50 ± 24.2
TS/PCL (20/80)	17.70 ± 0.6	401.60 ± 45.1
TS/PCL (30/70)	15.10 ± 1.3	406.60 ± 43.5
TS/PCL (40/60)	9.00 ± 0.6	297.80 ± 37.3
TS/PCL (50/50)	8.30 ± 0.7	276.80 ± 61.5
<b>Gelatinized starch (GS)</b>		
GS/PCL (0/100)	30.40 ± 4.60	613.40 ± 108.50
GS/PCL (10/90)	19.44 ± 3.00	388.97 ± 98.95
GS/PCL (20/80)	16.64 ± 0.95	394.19 ± 44.35
GS/PCL (30/70)	16.74 ± 0.95	396.65 ± 36.36
GS/PCL (40/60)	8.33 ± 0.47	132.48 ± 11.83
GS/PCL (50/50)	2.91 ± 0.39	2.20 ± 0.36

Values are the average of eight determinations ± SD.

Source: Chollakup et al., 1998

**Table 4. Physical properties of starch/PCL blends in the ratio of 30:70 using either granular (TS) or gelatinized starch (GS).**

	Tensile strength (MPa)	Elongation (%)
<b>Irradiated starch* and irradiated PCL* blend</b>		
1. Before radiation		
- PCL	53.6	972.8
- TS/PCL	16.5	403.8
- GS/PCL	8.9	166.1
2. After radiation		
- PCL*	31.9	678.0
- (TS/PCL)*	8.2	27.1
- (GS/PCL)*	9.2	13.5
<b>Irradiated starch* and PCL blend</b>		
1. Before radiation		
- TS/PCL	16.5	403.8
- GS/PCL	8.9	166.1
2. After radiation		
- TS*/PCL	12.0	383.6
- GS*/PCL	10.0	135.0



Source: Chollakup et al., 1999a.

Figure 7. Physical properties, determined as tensile strength and % elongation, of cassava starch and PCL blends with the inclusion of silk protein (silk hydrolysis-SH or silk fibroin-SF) at various concentrations (0 to 20%).

Source: Chollakup et al., 1999b.

**Table 5. Physical properties of PCL/partially hydrated starch (PS) and PCL/Hydrated starch (HS) at the ratio of 70/30 with various contents of sucrose ester (SE).**

	Tensile strength (MPa)	Elongation (%)
<b>PCL/PS</b>		
+ 0% SE	10.18 ± 0.95	217.28 ± 38.52
+10% SE	7.82 ± 0.98	176.94 ± 63.13
+15% SE	7.53 ± 0.58	200.59 ± 22.08
+20% SE	7.73 ± 0.79	197.39 ± 32.25
<b>PCL/HS</b>		
+ 0% SE	8.39 ± 0.68	125.22 ± 38.86
+10% SE	7.36 ± 0.82	157.29 ± 47.66
+15% SE	6.58 ± 0.50	124.59 ± 25.19
+20% SE	6.53 ± 0.28	134.74 ± 15.10

Source: Siroth et al., 1999.

## CONCLUSIONS

Cassava starch is the cheapest carbon source in the region and can be applied for the production of biodegradable plastics in the future in two different ways:

- a) As polymers: cassava starch can serve as a carbon source in the fermentation process leading to the formation of high molecular weight polymers, PHB etc., or organic acids such as succinic acid and lactic acid, which can subsequently undergo direct condensation to high molecular weight polymers. The future polymers will be from fermentation processes that give more consumer confidence.
- b) As the blending material cassava starch can be modified in different ways, so that the properties of the starch in the polymer blend are the best possible. This will lead to the most reasonable production cost.
- c) Through genetic engineering some plants are reported to have the ability for polymer production, such as a transgenic tobacco plant expressing a bioelastic protein-based polymer (Daniell and Guda, 1997). If biodegradable polymers could be synthesized in plants, like starch or lipid, the polymer's cost should be competitive with those from more conventional sources.

Despite the superior properties of conventional plastics, biodegradable plastics will be required in increasing amounts in certain markets. Major polymer producers are therefore increasing their research and development investments in this area.

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