PULSE CANADA

CASE STUDY

EVALUATION OF PEA STARCH FOR BIOPLASTIC APPLICATIONS



BACKGROUND

Traditionally, starch from cereal, root and tuber crops has played an important role as a food ingredient, but it is increasingly being used in other applications such as paper, pharmaceuticals, and textiles. Native starches from these crops generally exhibit high degradation rates, limited processability, and poor mechanical properties. Researchers have evaluated different methods to improve the functional properties of native starches to meet industry requirements for particular end-use applications. The advancement towards commercialization of biodegradable plastic has led to application of starch in two forms: granular (native or modified) form and thermoplastic (plasticized) form. Blending these starch forms with synthetic biodegradable and non-biodegradable polymers for biodegradable plastics has also been explored. Many factors have been reported to affect the performance of these bioplastic products, some of which include starch particle size, starch modification, amylose/amylopectin ratio, plasticizer, processing method and condition, reinforcement and compatibilizer. Despite extensive research in this area, most of these starch-based composites have not made it to the market owing to their inherent material deficiencies particularly in terms of strength and water resistance.

Research to date has been focused heavily on cereal and root/tuber crops including corn, potato and tapioca, but the growth of the pea fractionation industry in Canada presents a good opportunity to study pea starch. Peas are an environmentally sustainable crop. They are extremely effective at reducing greenhouse gas emissions due to their unique ability to sequester nitrogen. Not only do they require little to no nitrogen themselves, they "fix" nitrogen in the soil and help fertilize future crops. Research done by Pulse Canada shows that Canadian peas are one of the most sustainable crops in the world. Peas are a protein source with a very low water footprint, are well-adapted to semi-arid conditions and can tolerate drought stress. They also use water in a different way than other crops grown in rotation, extracting water from a shallower depth, leaving more water deep in the soil for the following year's cereal or oilseed crop.

There are two major categories of pea fractionation processing: wet fractionation produces a starch isolate (≥85% starch on a dry weight basis) and dry fractionation yields a starch-rich flour (<85% starch on a dry weight basis). Since the majority of the pea seed is comprised of starch (~45-48% dry weight basis), this is a significant co-product of pea protein yielded during the fractionation process. Given the growth in pea protein fractionation in Canada over the last decade and continued investments being made into the industry, significant volumes of pea starch available to be used in industrial applications including biodegradable plastics.

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PROJECT APPROACH

The objective of this project was to evaluate pea starch as a feedstock to make bioplastics for food packaging applications. The parameters studied include type of pea starch (isolates vs. concentrates), plasticizer type and concentration, and temperature of extrusion. Mechanical properties such as tensile strength, flexural strength, and elongation/strain were evaluated.

The research in this report was written and conducted by: Dr. Jianbo Lu, Nian Liu, Zhixiong Zhang, Jason En, Dr. Victor Cheng, and Hong Qi. Bio-Industrial Opportunities Section, Food and Bio Processing Branch, Alberta Agriculture and Irrigation.



THERMOPLASTIC STARCH (TPS) DEVELOPMENT

Native starches exhibit limitations related to mechanical integrity, thermal stability, and humidity absorption. Because of these limitations, starches are often blended with other materials to enhance their properties. Blending starches aims to reduce the production cost, improve barrier properties and dimensional stability, decrease hydrophilicity, and increase biodegradability. To optimize the overall properties of such blends, starches are blended with low molecular mass plasticizers such as glycerol, ethylene glycol, and water. In some instances, citric acid is also used as a co-plasticizer.

Pea starch materials were sourced by Pulse Canada. In this project, four different variables were tested and evaluated for their impacts on bioplastic properties:

- **Pea starch type:** isolated (~99% starch) vs. starch-rich flour (76.2% starch)
- **Plasticizers:** glycerin and ethylene glycol were tested as the main plasticizers while water and citric acid were tested as co-plasticizers. Either pure plasticizer or a mixture of plasticizer, water, and citric acid at a 4:1:1 ratio (by weight) (Figure 1) was injected into the extruder.
- **Inclusion of plasticizer:** plasticizer accounted for 40% or 50% of total mass of extrusion.
- **Extrusion temperature:** 100 °C versus 130 °C

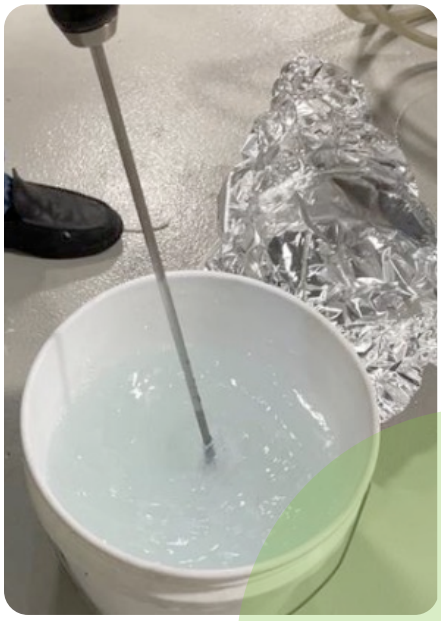


Figure 1. Co-plasticizer consisting of plasticizer (glyceron/ ethylene glyacol), water and citric acid at a 4:1:1 ratio.

COMPOUNDING AND EXTRUSION

The pea starch bioplastics compounding process was performed using a Century CX-40HT twin-screw extruder at the Bio Processing Innovation Center, AB. Pea starch was fed into the main feeding port at the beginning of the extrusion process and mixed with plasticizer via a calibrated injection pump at a designated rate. Both the starch feeder and the injection pump were calibrated for each type of pea starch and mixture of plasticizer before extrusion. The pea starch and plasticizer were compounded through the extruder at a screw rate of 170 rpm. Figure 2 shows the screw layout and processing profile while Figure 3 depicts pea starch strands being collected from the hot-faced die at the end of extrusion as well as the strand pelletizer. Strands were allowed to cool at room temperature before being cut into pellets using the strand pelletizer. The resultant bioplastic pellets, shown in Figure 4, were tempered in a 4 °C cooler for 1-2 weeks before being used for molding.

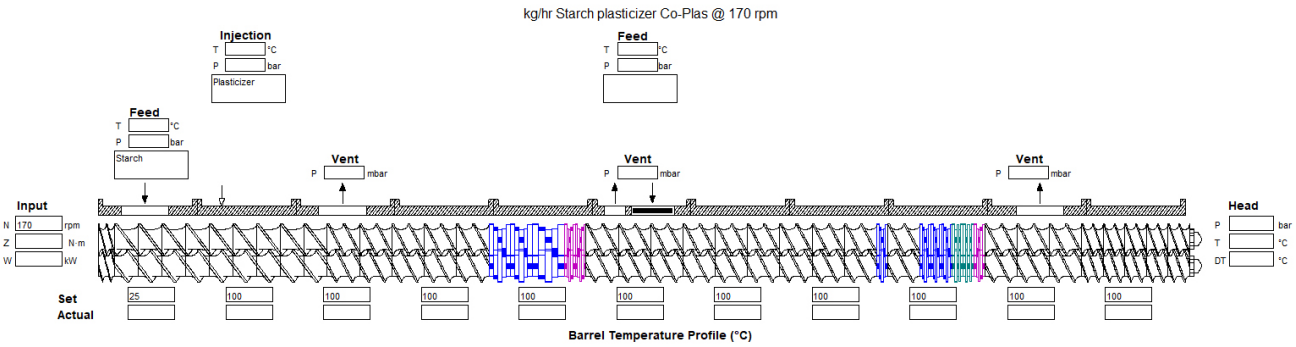


Figure 2. Screw layout and processing profile. Temperature shown at low-level conditions (100 °C) but was also set to 130 °C for high-level extrusion temperature.

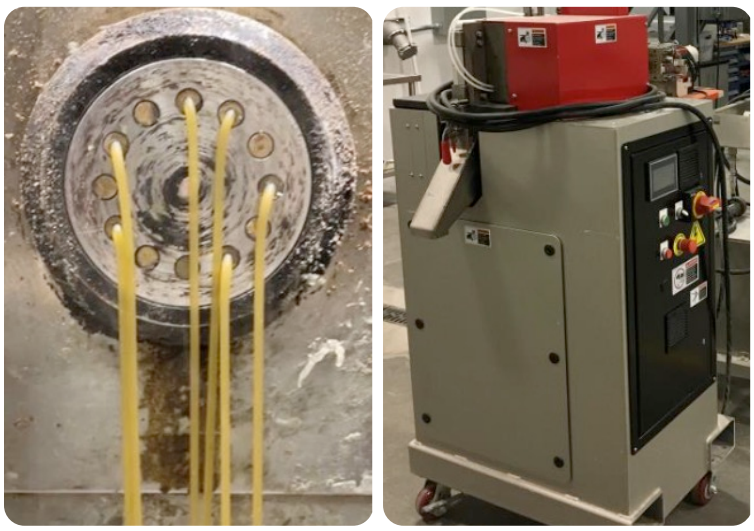


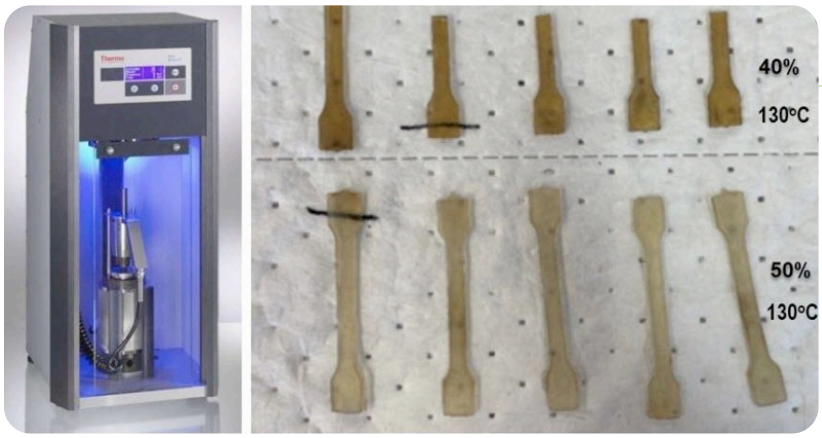
Figure 3. Strands of pea starch bioplastics from extruder die (left) and strand pelletizer used to cut strands into pellets (right)



Figure 4. Pellets of pea starch bioplastics. The top row is made from starch-rich flour while samples on the bottom row are made from starch isolate.

LAB INJECTION MOLDING

The starch pellets were molded using the Thermo Scientific™ HAAKE™ MiniJet Pro Piston Injection Molding System to form specimens for mechanical property testing (Figure 5). The melting temperature was controlled at 165 °C while the mold temperature and injection pressure were adjusted according to the type of bioplastic being tested. As shown in Figure 5, the specimens with low inclusion (40%) of plasticizer were harder and darker in color compared with those made using a high percentage (50%) of plasticizer. Figure 6 illustrates the transparency of the bioplastic specimen made using 60% pea starch and 40% plasticizer.



SPECIMENS WITH LOWER PLASTICIZER INCLUSION (40%) WERE HARDER AND DARKER COMPARED TO A HIGHER INCLUSION (50%).

Figure 5. Thermo Scientific™ HAAKE™ MiniJet Pro Piston Injection Molding System (left) used to produce samples for mechanical property testing (right). Samples on the top row contain 40% plasticizer whereas the bottom row contained 50% plasticizer. All samples shown were extruded at 130 °C.



Figure 6. Transparency of a 2.95 mm thick bioplastic specimen made from 60% pea starch and 40% plasticizer.

MECHANICAL PROPERTY TESTING

Mechanical properties such as tensile and flexural strength/strain were tested using an Instron. Tensile strength is a measure of the material's ability to resist deformation under tension or stretching forces. Elongation at break is a measurement that shows how much a material can be stretched—as a percentage of its original dimensions—before it breaks. Greater elongation indicates higher ductility. For tensile strength testing, ASTM D638 (Standard Test Method for Tensile Properties of Plastics), was performed by applying a tensile force to a sample specimen and measuring various properties of the specimen under stress (Figures 7 and 8). Flexural strength is the measure of a material's ability to resist cracking or breaking under bending stress. A material with high flexural strength has the ability to resist deformation when force is applied in tension or compression; it will inherently withstand bending, stretching, twisting, and other types of stress. ASTM D790-17 (Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials) was used to test flexural property which measures the stiffness of a material (Figure 9).



Figure 7. Tensile strength and elongation test by Instron

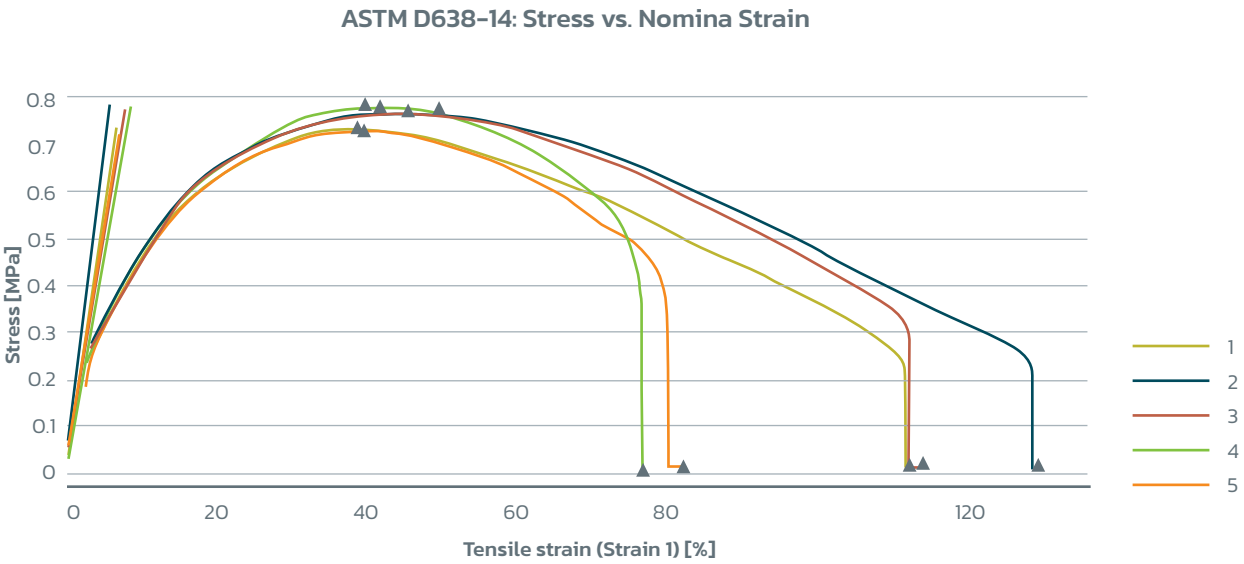


Figure 8. The tensile test of bioplastics made from 60:40 concentrated pea starch to plasticizer (4:1:1 glycerin:water:citric acid) extruded at 130 °C. The graph depicts the Instron results for 5 specimens of the sample type.

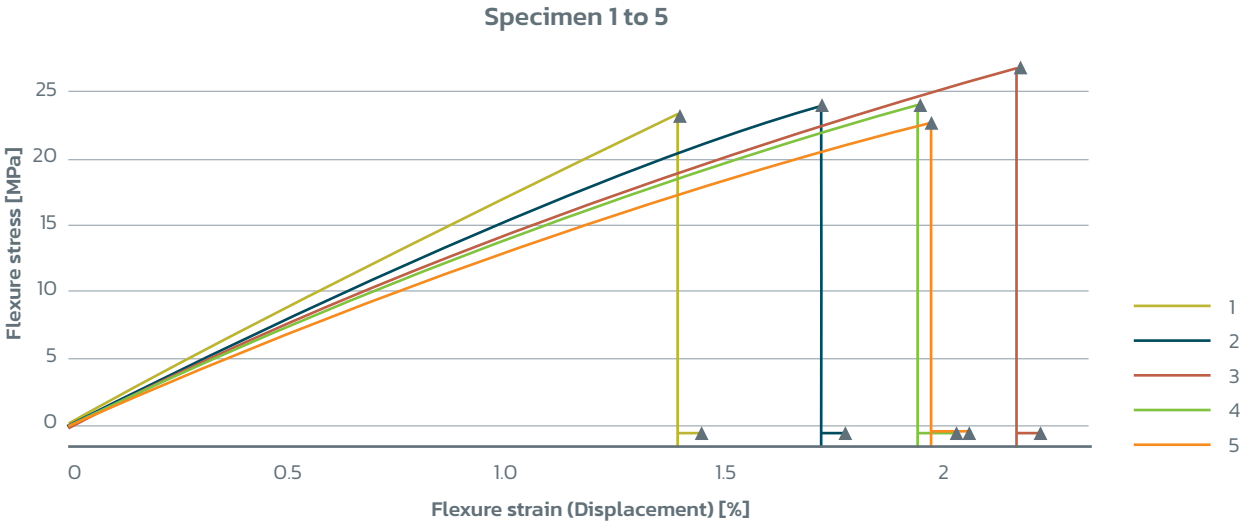


Figure 9. Flexural test of bioplastics made from 60:40 isolated pea starch to glycerin extruded at 130 °C. The graph depicts the Instron results for 5 specimens of the sample type.

The results of the mechanical property tests are summarized in Table 1. It was observed that most of the treatments presented impressive elongation and more rubber-like properties. However, these samples also had relatively low tensile strength and were too soft for the flexural strength test. Overall, only five samples with higher strength were capable of completing the flexural test.

Table 1 Summary of mechanical tests done by Instron to study tensile strength and flexural strain/elongation.

Starch	Plasticizer	Co-Plasticizer	Plasticizer Concentration (%)	Temperature (°C)	Tensile Strength (MPa)	Elongation at Break (%)	Flexural Strength (MPa)	Flexural Strain (%)
Starch Isolate	Glycerin	None	40	130	17.4	1.09	24.2	1.84
Starch Isolate	Glycerin	None	50	130	1.43	57.04		
Starch Isolate	Glycerin	None	50	100	2.4	39.89		
Starch Isolate	Glycerin	None	40	100	12.3	22.13	15.3	1.61
Starch Isolate	Glycerin	4:1:1	50	100	1.79	43.1		
Starch Isolate	Glycerin	4:1:1	40	100	3.82	0.18	5.31	0.296
Starch Isolate	Ethylen Glycol	4:1:1	40	130	0.17	46.04		
Starch Isolate	Ethylen Glycol	4:1:1	50	100	0.09	28.43		
Starch Isolate	Ethylen Glycol	4:1:1	40	100	0.23	39.67		
Starch Isolate	Ethylen Glycol	4:1:1	50	130	0.1	47.97		
Starch Isolate	Ethylen Glycol	None	50	130	0.1	18.35		
Starch Isolate	Ethylen Glycol	None	40	130	0.3	36.46		
Starch Isolate	Ethylen Glycol	None	50	100	0.1	17.81		
Starch Isolate	Ethylen Glycol	None	40	100	0.25	31.12		

Table 1 Summary of mechanical tests done by Instron to study tensile strength and flexural strain/elongation. *Continued...*

Starch	Plasticizer	Co-Plasticizer	Plasticizer Concentration (%)	Temperature (°C)	Tensile Strength (MPa)	Elongation at Break (%)	Flexural Strength (MPa)	Flexural Strain (%)
Starch-rich Flour	Glycerin	4:1:1	40	130	0.76	103		
Starch-rich Flour	Glycerin	4:1:1	50	130	0.27	74.03		
Starch-rich Flour	Glycerin	4:1:1	40	100	1.43	18.1		
Starch-rich Flour	Glycerin	4:1:1	50	130	5.75	43.39	1.74	4.99
Starch-rich Flour	Glycerin	4:1:1	40	130	2.89	1.48	15.9	1.55
Starch-rich Flour	Ethylen Glycol	4:1:1	50	100	0.19	6.07		
Starch-rich Flour	Ethylen Glycol	4:1:1	40	100	0.34	7.39		
Starch-rich Flour	Ethylen Glycol	4:1:1	50	130	0.21	41.45		
Starch-rich Flour	Ethylen Glycol	4:1:1	40	130	0.4	54.27		
Starch-rich Flour	Ethylen Glycol	None	35	100	0.65	38.93		
Starch-rich Flour	Ethylen Glycol	None	40	130	0.38	21.8		

STATISTICAL ANALYSIS

One way ANOVA was first used to determine whether there is a difference in performance between bioplastics made from pea starch isolate or starch-rich pea flour. Next, additional variables were introduced (plasticizer, co-plasticizer, extrusion temperature, or plasticizer inclusion) and two-factor ANOVA was applied to determine whether significant differences were observed. In general, a p-value ≤ 0.05 indicates statistical significance, a $0.05 \leq P \leq 0.10$ indicates marginal significance, and $P \geq 0.10$ indicates no statistical significance. The calculations were done with Excel and no post-hoc testing was carried out.

EFFECT OF STARCH TYPE

Bioplastics made from either starch type were tested for tensile strength and elongation. One-way ANOVA analyses of results indicated that there was no significant difference between the types of feedstocks used for both testing variables. **The results suggest either type of pea starch can provide similar strength and elongation properties in bioplastics.** This is useful information for future prototype development work as it rules out the importance of this variable.

EFFECT OF PLASTICIZER TYPE

When the plasticizer type was varied during compounding and extrusion, a significant difference ($p < 0.05$) in tensile strength between the resultant bioplastics was observed. **A lower tensile strength was generally observed for bioplastic samples that contained ethylene glycol as the plasticizer in comparison to those made with glycerin as the plasticizer.** This difference was more pronounced with the bioplastics made from starch isolates compared to those made from starch-rich flours. In terms of elongation, no significant difference was observed between pea starch bioplastics made with glycerin versus ethylene glycol as the plasticizer.

EFFECT OF CO-PLASTICIZER

A marginal difference ($p < 0.10$) was observed in the tensile strength of the bioplastics when a co-plasticizer was used compared to using plasticizer alone (i.e. glycerin or ethylene glycol). **In general, a lower tensile strength was observed by adding co-plasticizer to both types of starch samples.** No significant difference was found on elongation of pea starch bioplastics from co-plasticizer application.

EFFECT OF PLASTICIZER INCLUSION (%)

When bioplastics made with either 40% or 50% of plasticizer were tested for strength using the Instron, a marginal effect was observed (p-value = 0.108), although we consider this result to be somewhat significant. More experiments would be needed to determine whether the plasticizer inclusion percentage truly plays a role in determining pea starch bioplastic strength. **The tensile strength increased when plasticizer inclusion decreased from 50% to 40%, and this general trend was observed for bioplastics made from both starch types.** On the other hand, elongation of bioplastics made of either isolated or concentrated pea starch did not show any significant difference with different amounts of plasticizer included.

EFFECT OF EXTRUSION TEMPERATURE

Two extrusion temperatures (100 °C and 130 °C) were tested for impact on pea starch bioplastic properties. In the tensile strength test, no significant difference was observed between the two extrusion temperatures. **For the elongation test, a moderate difference ($p < 0.10$) was observed for bioplastics made at different extrusion temperatures, whereas a more pronounced effect was observed for samples made from starch-rich pea flour compared to isolated pea starch.**



SUMMARY

In this study, two different forms of pea starch–isolates and starch-rich flour–were evaluated as potential feedstocks to make bioplastics for packaging applications. The two types of pea starch were combined with different plasticizers and extruded at different temperatures to produce various bioplastic prototypes for testing. Statistical analyses were performed to better understand the results on mechanical properties such as tensile/flexural strength and elongation/strain.

- **Both pea starch isolates and starch-rich pea flour exhibited reasonable strength and elasticity required for use as a packaging plastic. Overall, no significant difference was observed when pea starch purity was varied, which suggests that either could potentially be used as a low-cost raw material for bioplastic production.**
- **When the plasticizer type and ratio, the co-plasticizer type, or extrusion temperature were varied, significant effects on mechanical properties of the bioplastic products were observed.**
- **High extrusion temperature, a relatively low plasticizer ratio and/or glycerin as a plasticizer resulted in prototypes with more strength.**
- **Low extrusion temperature, high plasticizer ratio and using ethylene glycol as a plasticizer resulted in prototypes with more elasticity.**

These insights will help us develop better formulations and processing parameters for specific packaging applications such as flexible film or rigid packaging. A more in-depth evaluation should be done in order to optimize formulation and processing parameters in order to produce a market-ready bioplastic. Citric acid as a co-plasticizer was also evaluated based on positive literature reports of preventing retro-degradation and further work is suggested for this area.



PULSE CANADA

www.pulsecanada.com
920–220 Portage Ave.
Winnipeg, MB
Canada R3C 0A5