

Agriculture and Agri-Food Canada | Agriculture et Agroalimentaire Canada

Canada

Development of plant protein-based bioplastic for industrial applications

Li, S.[1], Du, Y.[1], Thompson, M.[2], Zhang, Y.[1], Rempel, C.[3], Xiao, H.[4], Liu, Q.[1]

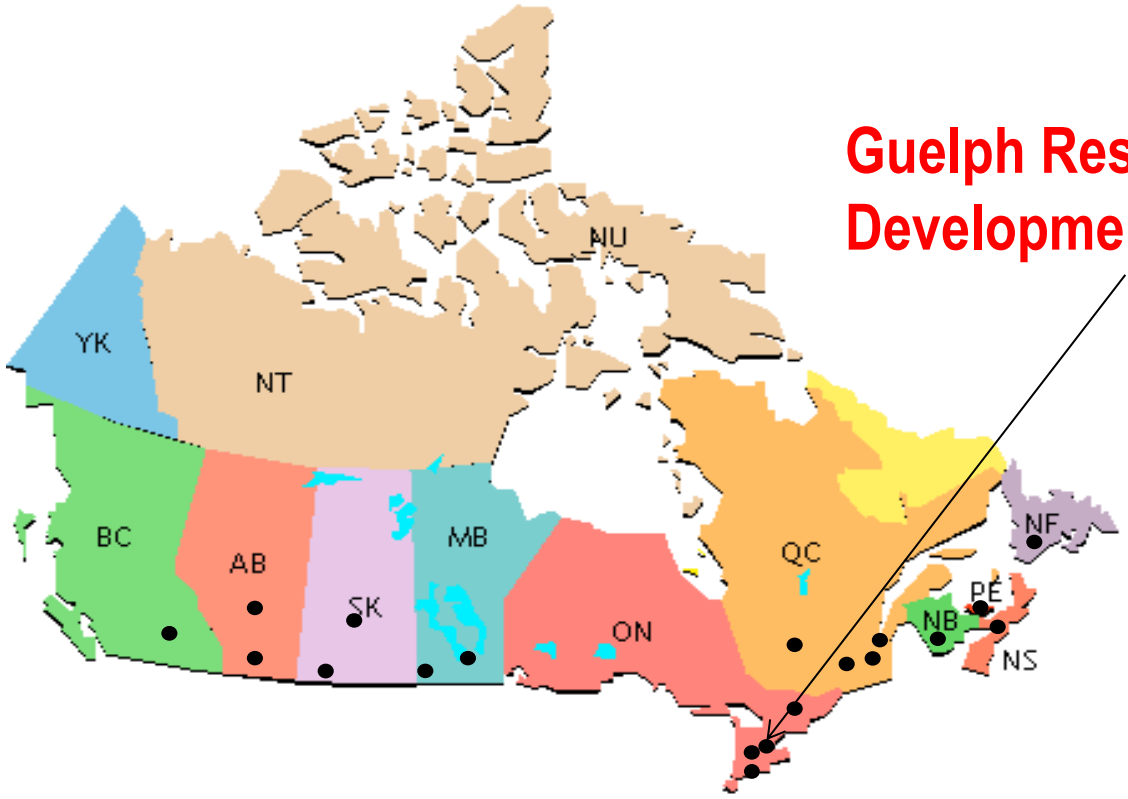
[1]Guelph Research and Development Centre, Agriculture and Agri-Food Canada
[2]Department of Chemical Engineering, McMaster University
[3]Canola Council of Canada, Winnipeg, MB
[4]Department of Chemical Engineering, University of New Brunswick

July 27, 2018

15th International Symposium on Bioplastics, Biocomposites and Biorefining

Agriculture and Agri-Food Canada (AAFC)

- 19 Research Centres across Canada
- ~300 scientists and ~1000 support staffs
- Annual budget of ~$300 million



AAFC



Consumer



Farm

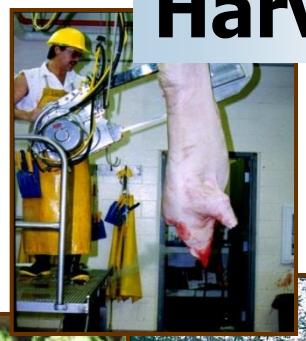




Transport & Storage

Ability to address research questions from production to consumption

Harvest









Processing

Motivation of this research

- Environmental white pollution issues (landfills, CO_2, etc.) from plastic
- Low cost, readily available (e.g. canola meal, a by-product from canola oil processing plant)
- Polymeric material that can be economically shaped
- Good compatibility with a broad range of hydrophilic materials (fibres, minerals, polymers, etc.)
- AIP Canola cluster support with funding (2014-2018)

Canola



Vegetable Oil





Canola Seed



Canola Meal (CM)



- CM consists of 36% crude protein

Cruciferin (12S globulin) and napin (2S albumin)

Livestock Feed



Modification of CM for Products

- Plastics
- Adhesives
- Composites

The targets of protein-based bioplastics

- Packaging films including bags, foams
- Molded articles including toys
- Disposable products including food trays
- Others















Weakness and challenges

- Poor processability
- Narrow processing window
- Poor mechanical properties
- Poor water resistance
- Poor antimicrobial activity

Protein modification (crosslinking)

- Aldehydes
- Thiol
- Polyurethane and Polyisocyanate
- Enzyme
- 1,2-Epoxy-3-chloropropane (ECP)
- 3-ethyl-carbodiimide hydrochloride (EDC) and Nhydroxysuccinimide (NHS)

Ref: Du et al. 2015. *Journal of Applied Polymer Science* 133 (17), pp. 1-13

How/What is Antimicrobial Biodegradable Packaging?

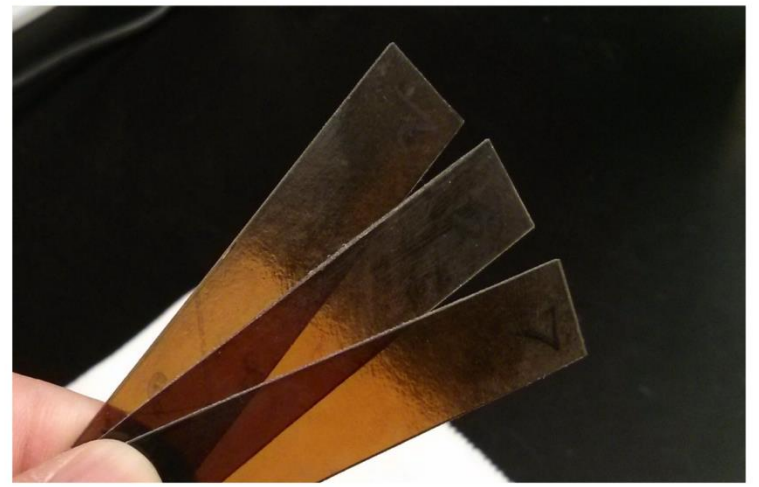
- Incorporation of the active phase by means of coating technique
- Use a biodegradable polymer as a carrier for antimicrobial agent, allowing safe and gradual release from the packaging to the food
- Check the effectiveness for antimicrobial food packaging purpose

Aims of the Research Work

- Improve the processability of plant protein-based bioplastics and bioproducts – Approach 1
- Modify protein to improve the functional properties - Approach 2
- Develop adjustable water resistance protein-based bioplastic film with long-term antimicrobial property - Approach 3

Potato protein-based bioplastics – Approach 1

- **Plasticizer effect**
  - Three plasticizers: glycerol, sorbitol, and PEG-400, were studied
- **Processes**
  - The effects of plasticizers on compression molding and extrusion processes were investigated
- **Pre-treatment or additive**
  - Alkali treatment of protein with and without reducing conditions for compression
  - Dry mixing with additives (e.g. sodium sulfite) for extrusion

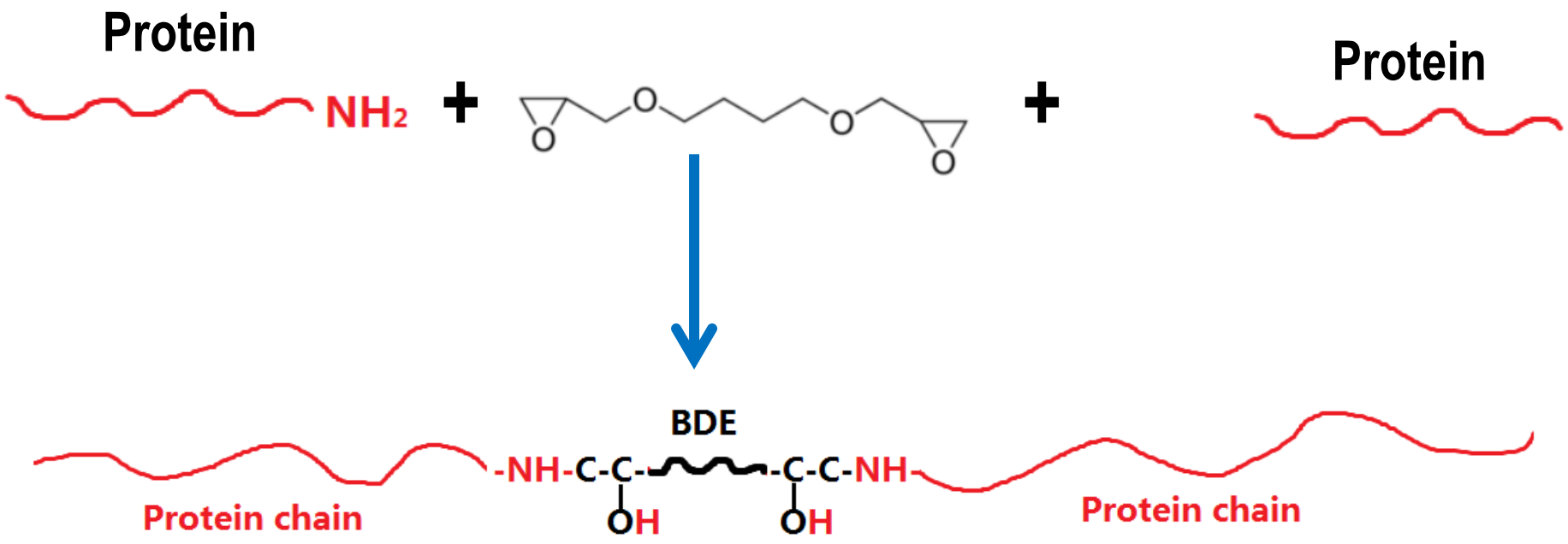


Summary – Approach 1

- ✓ The tensile strengths of potato protein-based bioplastic were 20-25 MPa
- ✓ The bioplastic can be designed to be brittle or highly ductile
- ✓ The alkali treatment changed the potato protein's tertiary and secondary structure and/or molecular weight that led to the change in static tensile properties and dynamic mechanical properties of potato protein-based bioplastics

Protein modification to improve the properties

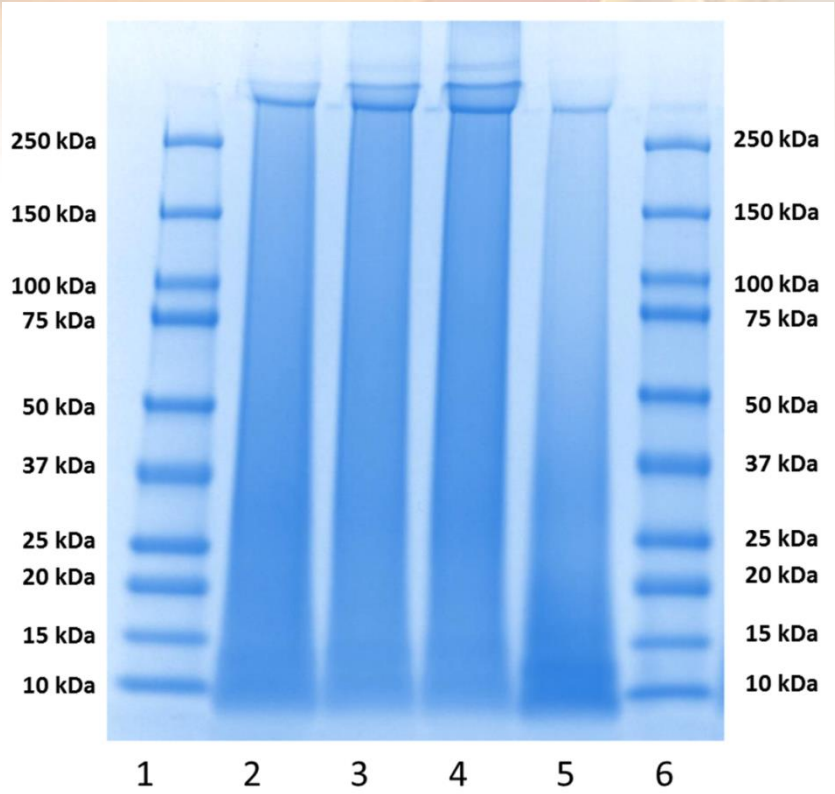
Approach 2: Novel branched/cross-linked canola protein isolate using 1,4-Butanediol diglycidyl ether (BDE) as cross-linker



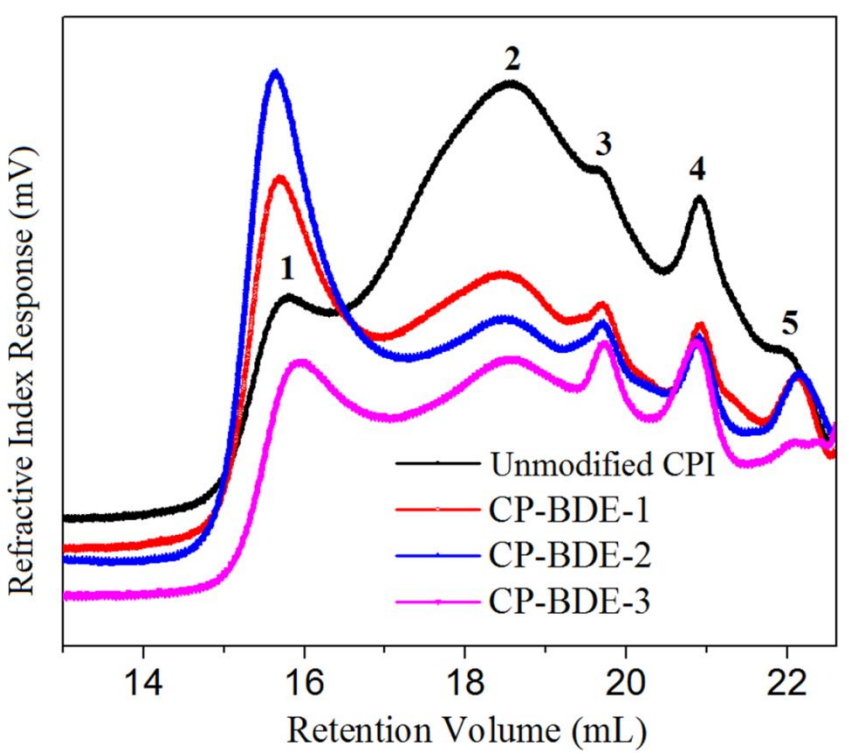
Ref: Li et al. 2017. *European Polymer Journal* 89: 419-430

Molecular structure of modified protein

SDS-PAGE



HPSEC



Lanes 1 and 6, molecular weight marker; lane 2, CPI-BDE-1; lane 3, CPI-BDE-2; lane 4, CPI-BDE-3; lane 5, unmodified CPI.

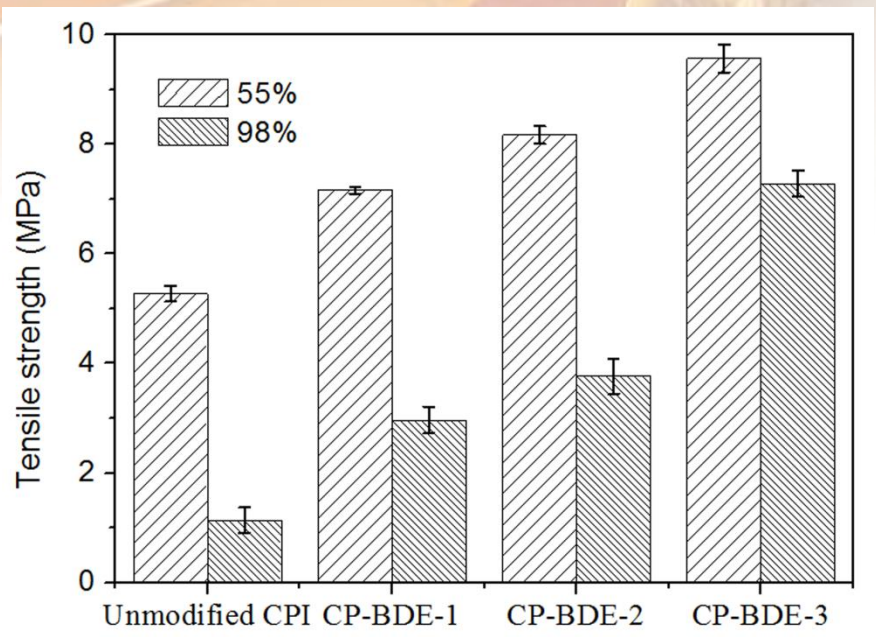
Ref: Li et al. 2017. *European Polymer Journal* 89: 419-430

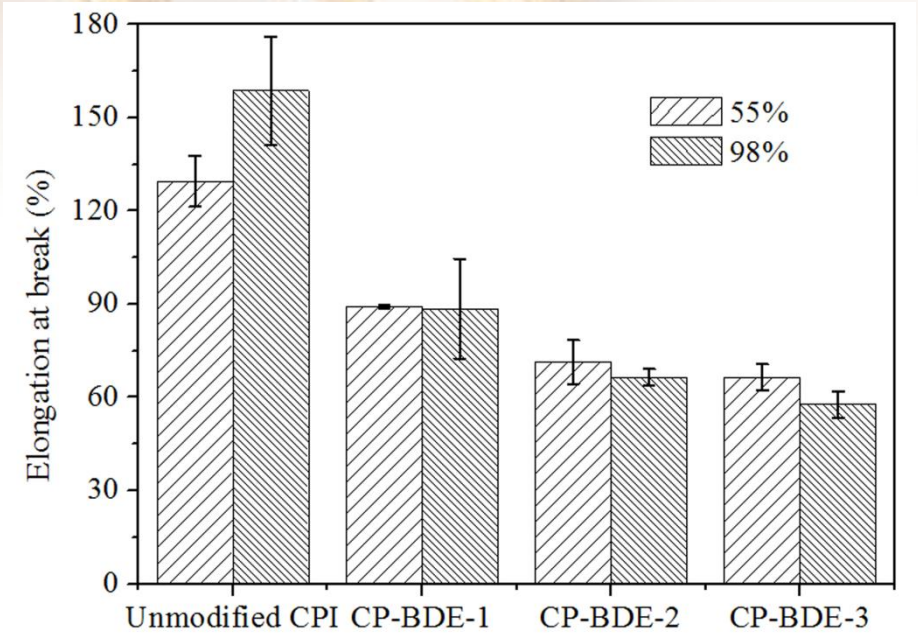
DMA and TGA data of modified CPI

Sample	α relaxation		β relaxation		Breakage temperature in TGA curve (° C)
	Peak temperature (° C)	tanδ at peak temperature	Peak temperature (° C)	tanδ at peak temperature	
Unmodified CPI	42.0	0.44	-50.9	0.24	281.7
CP-BDE-1	32.6	0.46	-50.5	0.24	294.3
CP-BDE-2	22.8	0.44	-48.0	0.25	304.5
CP-BDE-3	17.6	0.42	-47.8	0.25	309.2

Ref: Li et al. 2017. *European Polymer Journal* 89: 419-430

Mechanical properties





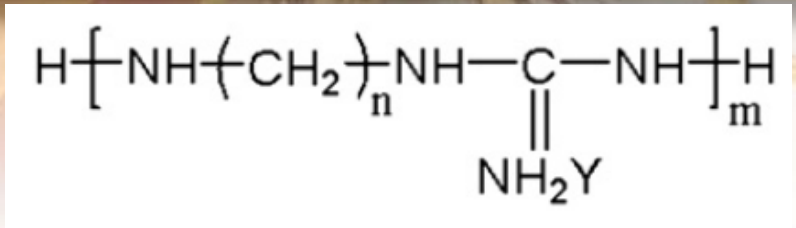
Tensile strength (left) and elongation at break (right) of unmodified and branched CPI films at conditioning humidities of 55 % and 98 %.

Ref: Li et al. 2017. *European Polymer Journal* 89: 419-430

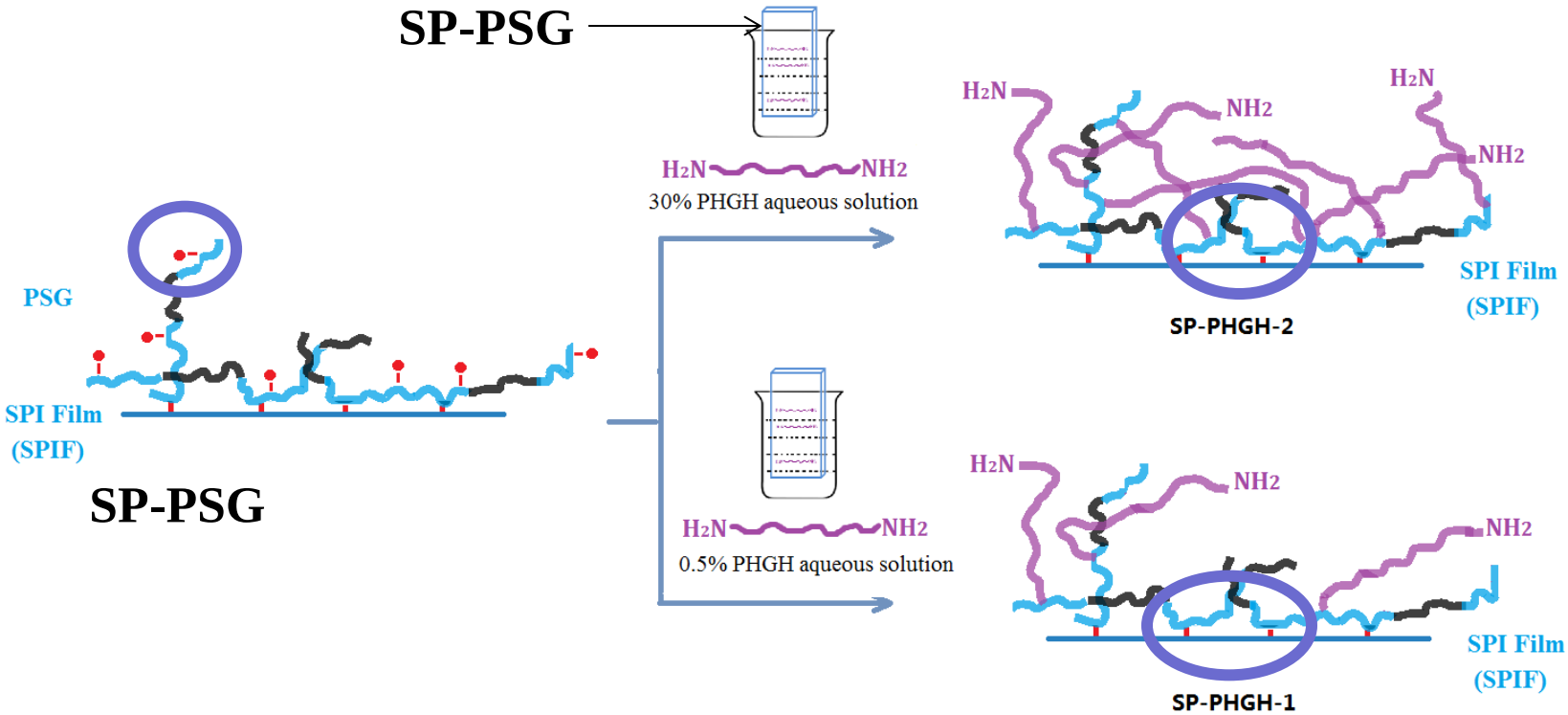
Summary – Approach 2

- ✓ Branched CPI was obtained by intermolecular instead of intramolecular coupling.
- ✓ Branching reaction took place among any protein fraction in native CPI.
- ✓ Branched CPI showed higher thermostability and tensile strength than native CPI.

Approach 3: Preparation of SP-PSG with PHGH

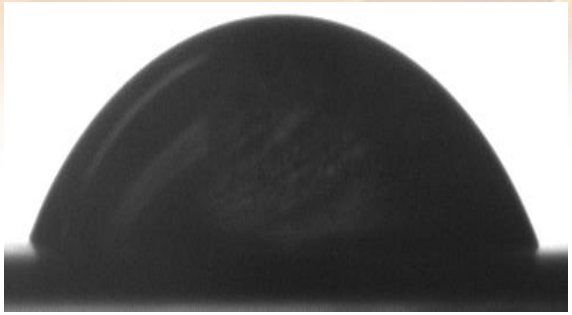


Poly(hexamethylendiamine-guanidine hydrochloride) (PHGH) – Antimicrobial polymer

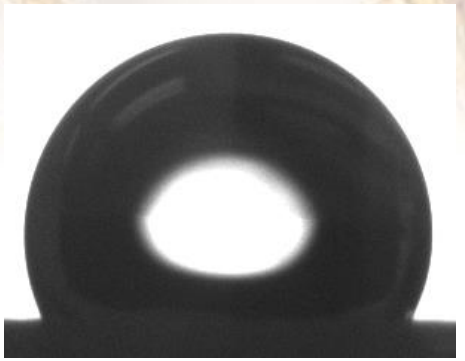


Ref: Li et al. 2016. *Materials Science and Engineering C* 69: 947-955

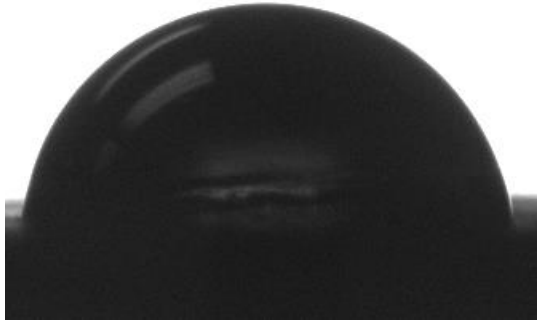
Water contact angle of film (SP-PSG-PHGH)



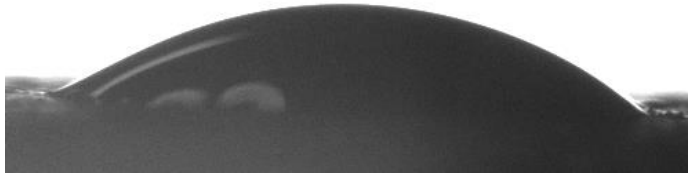
(a) native SPI film, 61.6°



(b) SP-PSG, 114.6°



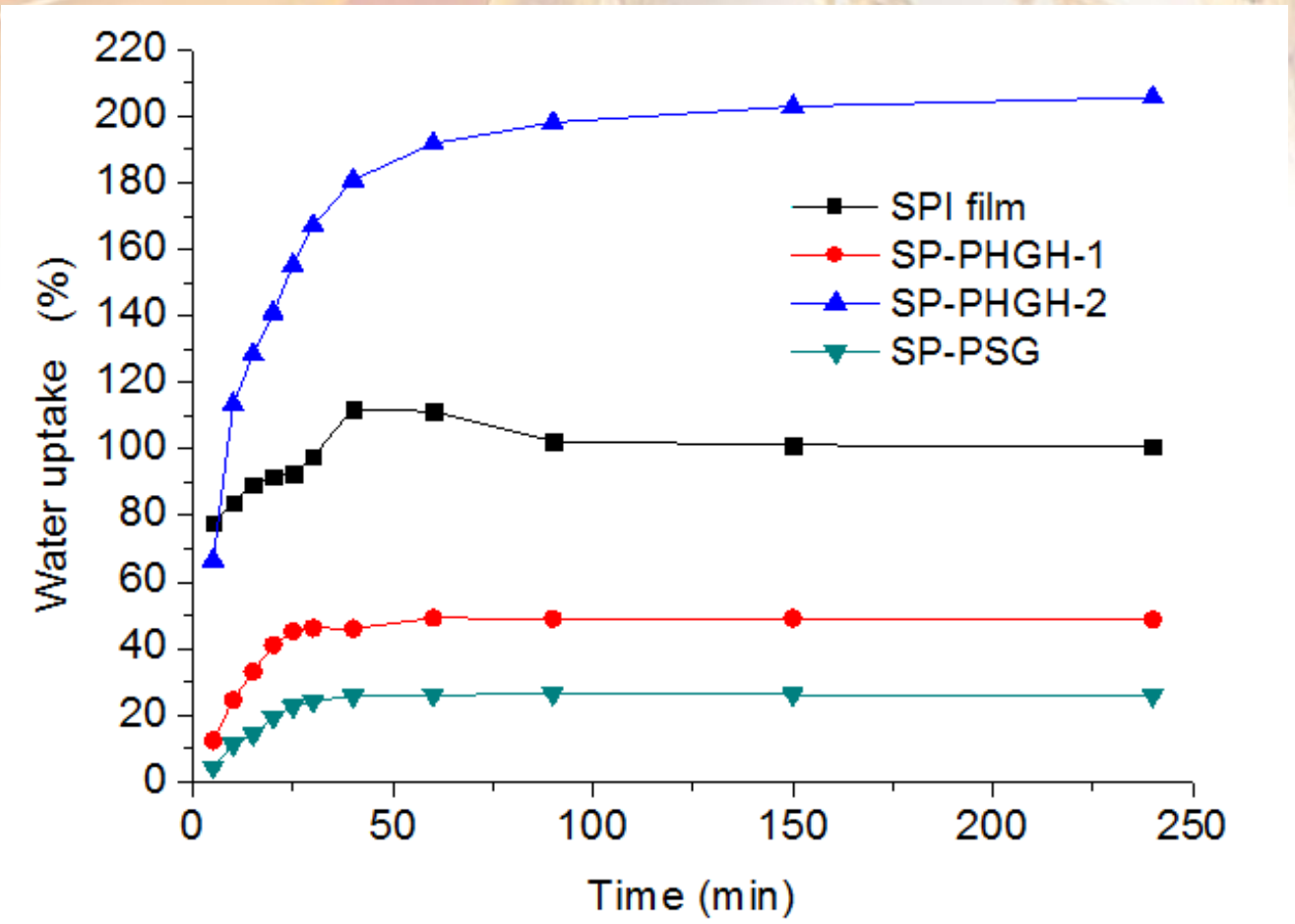
(c) SP-PHGH-1, 82.3°



(d) SP-PHGH-2, 36.4°

Ref: Li et al. 2016. *Materials Science and Engineering C* 69: 947-955

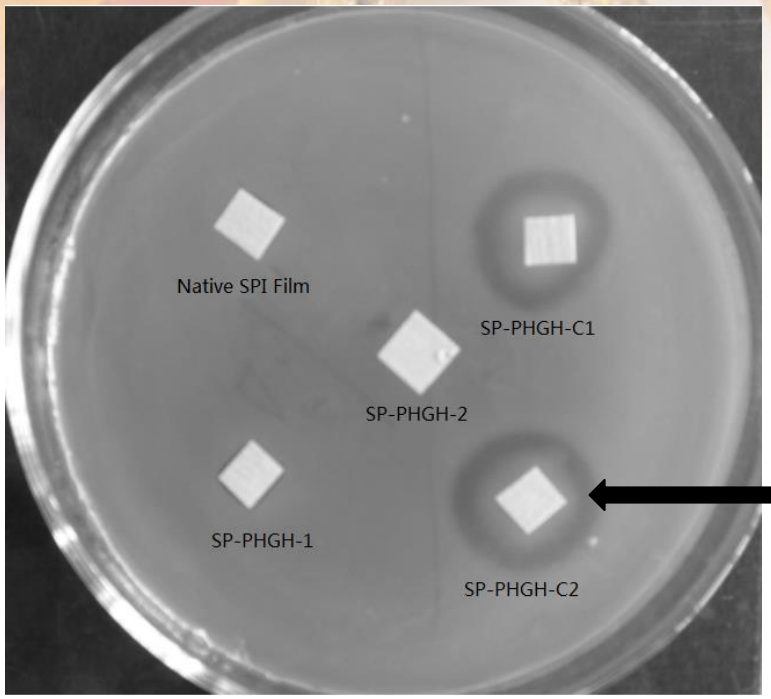
Water uptake



$$Water\ \ uptake\ (\%) = \frac{(W_t + W_s) - W_0}{W_0}$$

Ref: Li et al. 2016. *Materials Science and Engineering C* 69: 947-955

Diffusion antimicrobial activity



inhibition zone

Procedure:

1)Coat bacterial solution on agar plate,

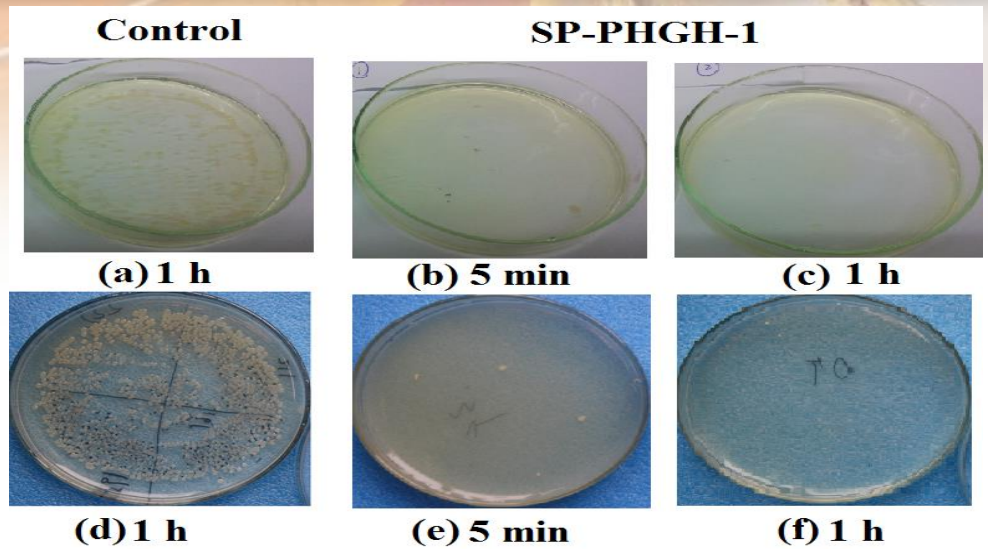
2)Place sample films on the bacteiral coating,

3)Incubate the bacteira at 37 C for 24 h.

C1, C2 samples obtained by immersing SPI film into 0.5% and 30% PHGH aqueous solution (no chemical bonding), respectively

Ref: Li et al. 2016. *Materials Science and Engineering C* 69: 947-955

Antimicrobial property of novel protein-based bioplastic film



Shake flask method was employed to evaluate antimicrobial activity against Gram-positive S. aureus (a, b, and c) and Gram-negative E. coli (d, e and f).

	At 5 min of contact			At 1 h of contact		
Microorganisms	Bacteria no. with control	Bacteria no. with SP-PHGH-1	% reduction	Bacteria no. with control	Bacteria no. with SP-PHGH-1	% reduction
s. aureus	**3.92×10^5**	**3**	**≥99.99**	**4.45×10^5**	**0**	**100**
e. coli	**2.87×10^5**	**4**	**≥99.99**	**3.56×10^5**	**3**	**100**

Ref: Li et al. 2016. *Materials Science and Engineering C* 69: 947-955

Summary

- ✓ By immobilizing different amounts of PHGH, a water resistance-adjustable protein-based bioplastic can be obtained
- ✓ The immobilization of PHGH offers surface antimicrobial activity by contact killing
- ✓ The incorporation of PHGH by chemical bonds decreases the risk of this antimicrobial agent leaching, which does potential harm to the environment and the human body
- ✓ Novel film has a potential applications in food packaging and medical fields

Acknowledgement

- Mrs. Elizabeth Donner, Mr. Zhanhui Lu (AAFC research technician) for their technical support
- Ms. Kristi Ciardullo, McMaster University; Ms. Brianna Ball , University of Guelph, for conducting some research experiment
- AAFC Funding through Science Reporting and Competitive Sector (A-base)
- GF2 Canola/Flax Science Cluster funding for AIP CL-08 project


Thank you!
Canada