Master's Thesis Engineering Technology

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Development of a functional carrageenan film through crosslinking techniques employing glucono-δ-lactone and chitosan

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Situating & Objectives

Packaging is essential in the food industry for preserving food, maintaining safety, and safeguarding integrity. Although it reduces food waste and is vital to the supply chain, packaging also poses challenges like waste accumulation, contaminant migration, cost issues, and energy consumption. Biodegradable and biobased polymers, including seaweed polymers like carrageenan (CAR) and sodium alginate, offer promising alternatives for eco-friendly packaging, leveraging seaweed's environmental advantages such as minimal resource requirements and carbon sequestration [1]. Despite the potential of seaweed polymers, their water sensitivity remains a concern, necessitating blending with other materials or crosslinking to improve performance without compromising biodegradability [2]. By exploring these innovative approaches, this research aims to reduce the water sensitivity whilst maintaining mechanical strength through crosslinking with glucono-δ-lactone (GDL) (Fig. 2) and chitosan (CS) (Fig. 3) which both show less hydrophilic properties compared to CAR. The combination of CAR, GDL and CS has not been tested before in literature.

Methods

Film synthesis

- Production of reference and crosslinked films using crosslinking techniques shown in figure 2 and 3
  - Reference films only contain CAR, CAR-CS, CAR-GDL no combination of all three
- Box-Behnken design for response surface methodology (RSM) varying the w/v% of CAR, CS and GDL (15 films of which 3 center points
  - Ranges defined during preliminary phase

Table 1: Properties of Box-Behnken design experiment

Factors	Symbols	Levels (%(w/v))		
		−1	0	+1
Carrageenan	CAR	1.00	1.75	2.50
Chitosan	CS	0.50	1.25	2.00
Glucono δ-lactone	GDL	0.50	1.50	2.50

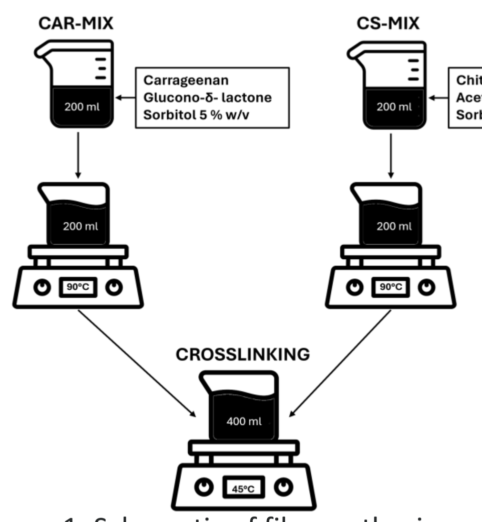

Figure 1: Schematic of film synthesis procedure

Crosslinking

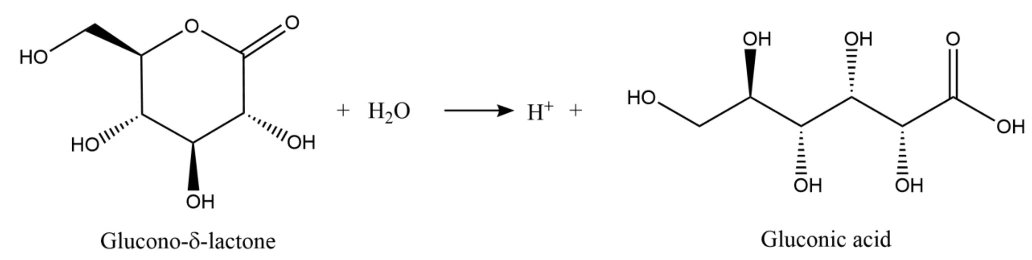

Figure 2: The hydrolysis reaction of GDL, which enables it to act as a proton donor for CS.

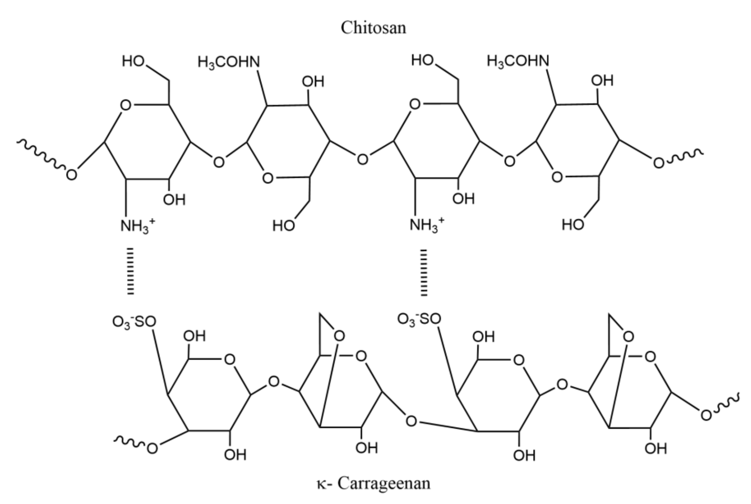

Figure 3: Molecular structure of CAR and CS and possible crosslinking interactions

Film casting

- Poor 100 ml into plastic mold
- Condition at 20°C and 50% RH or room conditions for 24 hours.
- Condition at 25°C and 30% RH for at least 24 hours before doing any tests.

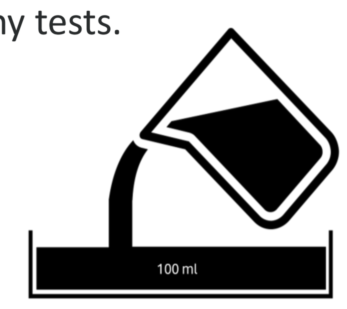

Figure 4: Casting procedure scheme

Characterization

- To determine the optimal equilibrium between mechanical properties and water sensitivity
- Mechanical properties (Tensile strength + elongation) → Tensile tester
- Water sensitivity → Contact angle (CA)
- Thermal stability →Thermogravimetric analysis (TGA)
- Functional group analysis → Fourier transform infrared spectroscopy (FTIR)
- Color analysis → Colorimeter

Results

RSM

- Complex interactions cause lower than expected tensile strength
- Increased elongation, compared to literature
- Optimal film derived from RSM: CAR2.50-CS2.00 -GDL1.5

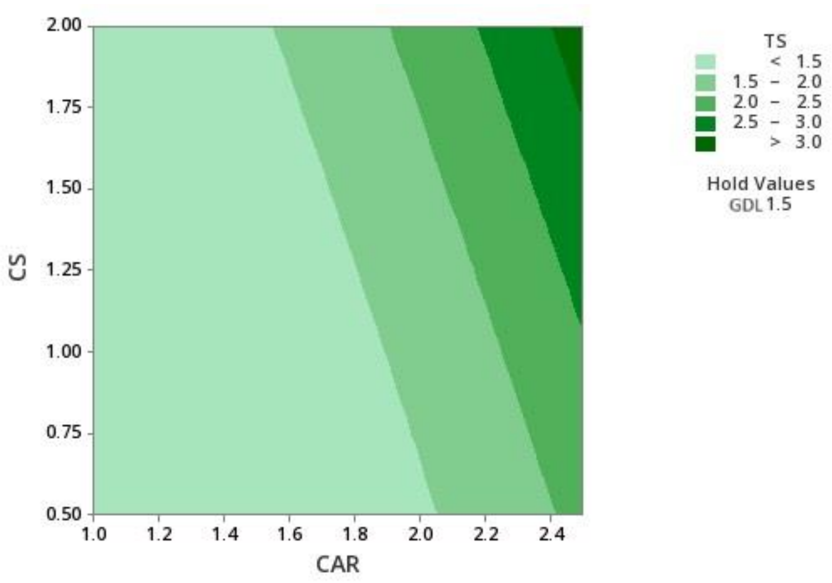

Figure 5: Contour plot of the impact of CS and CAR on Tensile strength (TS) in MPa

Contact Angle

- Samples with the addition of crosslinkers showed an increase CA compared to the CAR2.00 reference film.
- A blend of the three components exhibited lower CA compared to mixtures containing only CAR-CS or CAR-GDL, suggesting complex interactions.
- Optimal mechanical film by RSM resulted in a CA of:
  - 40.68° ± 2.22°

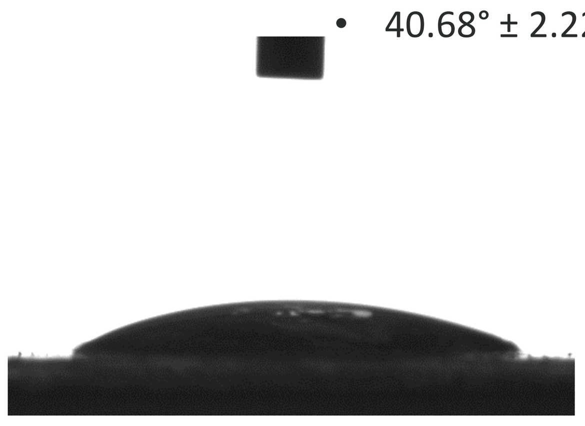

Figure 6: CA measurement of CAR2.00 reference film

36.30° ± 3.21°

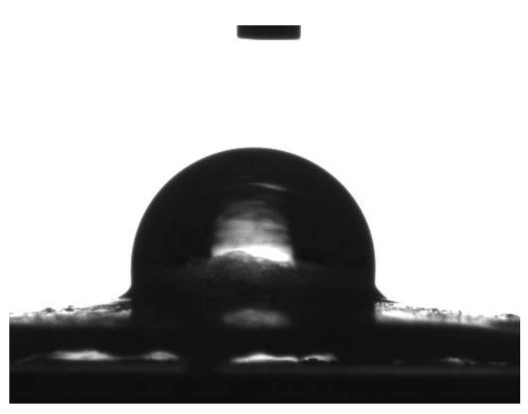

Figure 7: CA measurement of CAR2.00-CS1.00 reference film

106.46 ± 12.80°

TGA

- Increased thermal stability and lower decomposition rate after adding in crosslinkers GDL and CS into CAR-film
- Optimal film derived from RSM on mechanical properties showed the highest thermal stability

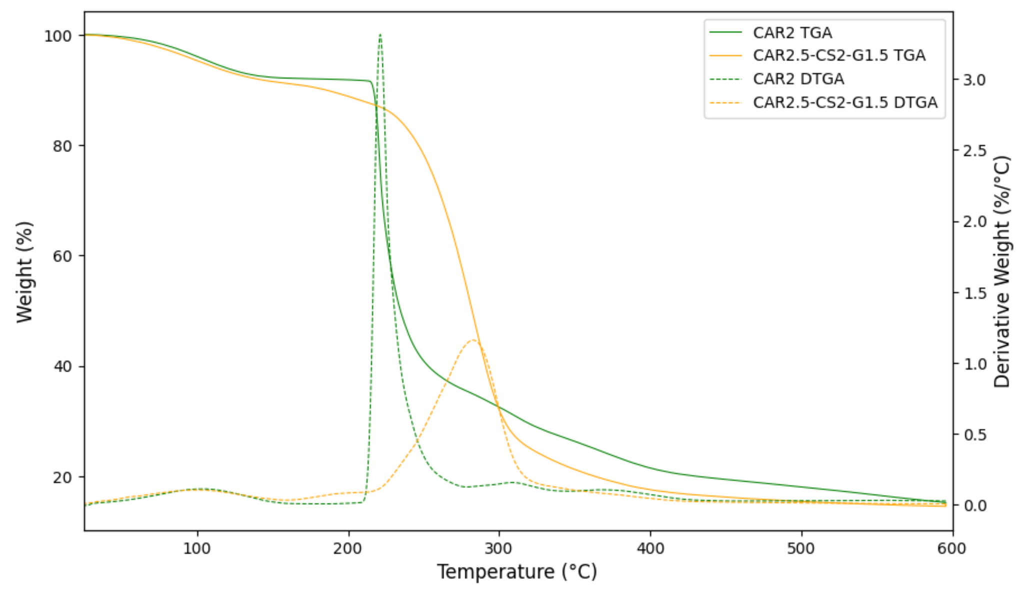

Figure 8: TGA results of CAR2 REF film and the optimal film using RSM

Conclusion

Lower tensile strength in reference and crosslinked films compared to the literature, suggests potential issues with the mixing method or the quality of the biopolymer itself. Different trends with varying concentrations of crosslinkers suggest complex interactions between the three molecules (CAR, CS, and GDL) and show the need for extra research. Although FTIR analysis confirmed the structures of individual components, the film-making process masked the characteristic peaks of CAR and CS, hindering the assessment of their interactions within the final film. Thermal stability improved with higher contents of all three components (CAR, CS, and GDL) after crosslinking as expected. Color analysis revealed a trade-off, with increased water resistance from CS at the cost of reduced film transparency. Overall, the study highlights the potential for carrageenan films with tailored properties through optimized formulations. However, further research is needed to address unexpected results, refine mixing methods, and achieve the desired balance of film properties for specific applications.

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References : [1] D. Pacheco, J. Cotas, J. C. Marques, L. Pereira, and A. M. M. Goncalves, Seaweed-Based Polymers from Sustainable Aquaculture to "Greener" Plastic Products, pp. 591–602. 2022.
[2] C. Lim, S. Yusoff, C. Ng, P. Lim, and Y. Ching, "Bioplastic made from seaweed polysaccharides with green production methods," Journal of Environmental Chemical Engineering, vol. 9, no. 105895, 2021.

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