Effect of Carboxymethyl Cellulose (CMC) on the Physico-Chemical Properties of Masa/Water Mixtures

By

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Why are we interested in CMC?

- Tortillas are the fastest growing segment of U.S. baking industry.

- Tortilla industry is the largest consumer of food-grade CMC. CMC is the most expensive ingredient in corn tortillas.

- CMC is added for shelf-life extension and to maintain a pliable texture.

- The mode of action of CMC in tortilla is unknown.
Objectives

- Characterize the effect of different quantities of CMC on unheated masa/water mixtures during storage using thermoanalytical techniques.

- Characterize the state of water and starch in heated masa/water mixtures with varying CMC’s and water contents using thermal analysis techniques during storage.
Background:
Structure of CMC

- Unit structure of cellulose

- Idealized unit structure of CMC with a DS (degree of substitution) of 1.0 (DS Generally in the range of 0.65-0.9)
Background
Masa and corn tortillas

Masa (Nixtamalization)
- Cooking → Steeping → Washing → Stone-grounding
  (corn and limestone solution)
- Milling ← Dehydration

Corn tortillas making
- Dry masa+water → Sheeting → Shaping
- Cooling and Packaging ← Baking
Background
DSC-Differential Scanning Calorimetry

DSC works by comparing the rate of heat flow of a sample to an inert material as both are heated or cooled at a programmed rate.
DSC 2920 (TA Instruments, New Castle, DE)
Background

TGA-Thermogravimetric Analysis

TGA measures the amount and rate of weight change in a material as a function of temperature or time.

TGA 2950 (TA Instruments, New Castle, DE)
Materials and Methods

A: Thermal Analysis

Dry Masa + gum → Heated: 10% PE31FGS CMC, PE32FGS CMC & guar gum

Dry ingredients with 50% & 60% DI H₂O → Sampling

DSC (U/H): 10-14 mg mixtures were placed into aluminum hermetic (High volume) DSC pans

DSC (Heated): Scanned from -50°C to 165°C @ 5°C/min

Stored for 0-14 days @ 4°C → Thermal Analysis

DSC (U/H): scanned from -50°C to 110°C (210°C) @ 5°C/min at day 0~14.

TGA (U/H): scanned from RT to 200°C @ 20 °C/min with a resolution of 3.0 and sensitivity of 2.0 at day 0~14.
Materials and Methods
B: Water Holding Capacity

5 g dry materials + Distilled water

centrifuge 2000g, 10 min

Approx WHC

Determination of WHC

Masa+0%, 0.5% or 1% 7MF CMC = 5g

Masa+10% gums =5g (31, 32, guar)

(Weight of tube+5.0+H2O)-(Weight of tube +5.0)

5

WM (g)=15/(Approx WHC+1)

Dry material +H2O

centrifuge


+1.5ml +0.5ml -0.5ml -1.5ml

Average the numbers of the two adjoining tubes that one with and one without supernatant, and divided by weight of material.
Materials and Methods
B: Water Holding Capacity (Heated)

5 g dry materials + excess DI H₂O

4.5 g dry masa + 10% (0.5 g) gum. (PE31FGS CMC, or PE32FGS CMC or Guar)

Gelatinization (100°C, 10 min)

Storage (4°C)

Centrifuge at day 0, 2, 6, 14. (2000 g, 10 min)

WHC (g) = Weight of sediment – 5
**Materials and Methods**

**C: Viscosity Measurement**

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**Moisture determination**

5 g gum heated in vacuum oven at 105°C for at least 3 hours (PE31FGS CMC, PE32FGS CMC, guar)

% MC in gum: \( \frac{(5 - \text{dry gum weight})}{5} \times 100\% \)

**Solution Preparation**

\( \text{H}_2\text{O} = \text{Weight of undried gum} \times (99 - \text{mc of gum}) \)

gum + \( \text{H}_2\text{O} \) (1% solution)

Agitated at 27.0*1000 rpm For 2 hours using Polytron PT 3100

**Viscosity measurement**

Placed into water bath at 25°C for 1 Hour prior to the measurement

Viscosity measured by Brookfield Digital Viscometer Using Spindle No 3 at 30rpm
Results and Discussions (unheated)

DSC results: Typical DSC thermogram

- Amylopectin melting
- Ice melting
Results and Discussions (unheated)

DSC results: Effect of CMC on % FW

For each mixture, during entire storage time, no significant difference observed. (all p values > 0.05)

50% mc:
FW in control > Others at day 0&14. (All P<0.05)

60% mc:
Gum addition had no impact on % FW (all p>0.05)

For each mixture, during entire storage time, no significant difference observed. (all p values > 0.05)
Results and Discussions (unheated)

DSC results: Effect of CMC on starch recrystallization.

CMC addition, storage time and moisture content had no significant impact on amylopectin recrystallization.
Results and Discussions (unheated)

TGA results: Typical TGA thermogram.
Results and Discussions (unheated)

TGA results: Effect of CMC on water distribution

CMC addition causes water distribution to be more heterogeneous.

Storage time:
- 50%mc control: no change
- 50%mc+ CMC: more homogeneous
- 60%mc control: more heterogeneous
- 60%mc+CMC: no change

Moisture content:
- Day 0: No impact.
- Day 14: Higher mc causes water distribution to be more heterogeneous.
Results and Discussions (unheated)

WHC results: Effect of CMC on water retention

Significantly larger amount of water were retained in the presence of CMC (p=0.0109).

No significant difference (p=0.7502) in WHC between the CMC concentration used (0.5 & 1.0%).
Conclusions (unheated)

- CMC addition at certain level (0.5%) may increase water retention, decrease % FW (50%mc), cause water distribution more heterogeneous but no impact on starch recrystallization in the unheated mixtures.

- Storage time had no significantly impact on % FW and amount of amylopectin recrystallization.

- Higher MC resulted in an increasing FW content, and more heterogeneity of water distribution (Day 14).
Results and Discussions (Heated)

Viscosity of each 1% gum solution

![Bar graph showing the viscosity of PE31FGS CMC, PE32FGS CMC, and Guar gum solutions. The graph indicates that PE31FGS CMC has the lowest viscosity, while PE32FGS CMC and Guar gum have higher viscosities.](image-url)
Results and Discussions (Heated)

DSC results: FW and UFW at day 0

50% mc: p=0.0000
FW in Control > Others

60% mc: p=0.0984
No significant difference in FW obtained.
Results and Discussions (Heated)

DSC results: Effect of gums on % FW

50%mc:
During storage, only FW in control decreased significantly (p=0.004).
(Other P values >0.05)

60%mc:
During storage, only FW in samples with 10% PE31FGS CMC decreased significantly (p=0.0418).
(Other P values >0.05)
DSC results: Effect of gum addition on amylopectin recrystallization

Gum addition had no impact on the melting enthalpy of recrystallized amylopectin. (all p>0.05).

The melting enthalpy increased with storage time.

Moisture content affected the melting enthalpy. Certain MC (50%) provides optimum conditions for starch recrystallization.
Results and Discussions (Heated)

WHC results: Effect of gums on water retention

Gum addition increased WHC and related to gum’s viscosity.
Results and Discussions (Heated)

WHC results: Effect of gums on water retention during storage

Gum addition increased WHC throughout storage.

WHC in control sample and sample with guar gum decreased significantly. (p=0.0001/p=0.005)
Examples of results and discussions, heated.

TGA results: Effect of gums on water distribution

A: The rate of weight loss showed a bimodal distribution in all samples with or without gum addition at day 0.

B: After storage, both 50%mc & 60%mc samples lost water more homogeneously (single curve)
Conclusions (heated)

- Gum addition increased WHC and “unfreezable” water (in 50%mc) in heated masa/water mixtures.

- FW content in most samples did not change during storage. Water distribution became more homogeneously after storage.

- Recrystallization of amylopectin as storage time, Certain MC (50%) provides optimum conditions for starch recrystallization. It was not affected by gum addition.

- These results seem to indicate that lack of flexibility in tortillas may have more to do with water redistribution and possible changes in amorphous phase than amylopectin recrystallization.
Future Work

These results need to be verified on a molecular level with such techniques as Nuclear Magnetic Resonance (NMR) spectroscopy.
Questions?

Thanks!