Salt–Starch Interactions as Evidenced by Viscosity and Dielectric Property Measurements

C. Bircan and S. A. Barringer

ABSTRACT

Increasing the concentration of salt (NaCl) or starch in a salt-starch solution depressed the dielectric constant and loss factor relative to a pure salt solution, except for the loss factor when no salt was present. The addition of salt to a starch solution increased the viscosity. Both viscosity and dielectric properties were decreased by mechanical agitation and by action of amylase. Above 10% starch the decrease in dielectric loss was abrupt, corresponding to the increase in viscosity. The changes were hypothesized to be due to an interaction between salt and starch, either through direct binding of the salt, or indirectly through the increase in viscosity.

Key words: dielectric properties, viscosity, starch, microwave, salt

INTRODUCTION

DIELECTRIC PROPERTIES DETERMINE THE RESPONSE OF A MATERIAL TO AN ELECTROMAGNETIC FIELD, SUCH AS OCCURS IN A MICROWAVE OVEN. THE INABILITY OF THE MOLECULES TO INSTANTANEOUSLY ALIGN WITH THE APPLIED ELECTROMAGNETIC FIELD LEADS TO DISSIPATION OF ELECTROMAGNETIC ENERGY. THE DIELECTRIC PROPERTIES REFER TO A COMPLEX NUMBER CONSISTING OF A REAL PORTION (THE DIELECTRIC CONSTANT OR \( \varepsilon' \)) AND AN IMAGINARY PORTION (THE DIELECTRIC LOSS FACTOR OR \( \varepsilon'' \)). THE DIELECTRIC CONSTANT IS AN INDICATION OF THE POLARIZABILITY OF THE MOLECULES AND THEIR ABILITY TO STORE ELECTRIC ENERGY. THE DIELECTRIC LOSS FACTOR IS RELATED TO THE ENERGY ABSORPTION AND DISSIPATION OF ELECTROMAGNETIC ENERGY FROM THE FIELD (Decareau, 1985).

In food samples, water and salt are the two major ingredients which influence dielectric properties. Other food components usually have a minor influence on the dielectric properties. Such factors which may affect dielectric properties are the electromagnetic field frequency and sample temperature. Water and salt content, frequency and temperature are commonly included in predictive equations, such as those of Sun et al. (1995) and Calay et al. (1995). The physical state of the food is not included in these equations, though it may influence the mobility of water and salt, which in turn may affect the dielectric properties.

It has been reported that changes in physical state affect dielectric properties. Umbach et al. (1992) found changes in both the dielectric constant and loss factor after the heating of gluten protein-starch mixtures. Barringer et al. (1995) reported changes in the dielectric loss of whey protein solutions after denaturation. Bengtsson et al. (1963) had indicated that the dielectric properties changed as the electromagnetic field was oriented perpendicular or parallel to meat fibers. Miller et al. (1991) found that changes occurred in the dielectric loss during starch gelatinization. In contrast to what would be expected from that work, Rynnenen et al. (1996) found no significant difference in dielectric properties between gelatinized and ungelatinized starches. Anantheswaran and Liu (1994) examined the effects of viscosity on heating rate in a microwave oven, including the effects of viscosity changes on convection currents in samples with similar dielectric properties.

Our objective was to determine whether interactions between starch and salt would affect the viscosity and dielectric properties of starch slurries.

MATERIALS & METHODS

SOLUTIONS OF HYDROXY PROPYLENE AND PROPYLENE OXIDE MODIFIED CORN STARCH (Amalean II, Cerestar USA, Inc., Hammond, IN) were prepared on a wt/wt basis. The starch-water solutions were blended in a Waring blender (Model 31L92, Waring Products Inc. New Hartford, CT) at low speed for 5 min followed by high speed for 10 min. After blending, the starch solutions were held at room temperature (23°C) to continue hydrating for 15-20 min before taking the dielectric measurement. Solutions with salt were prepared by adding 3% NaCl wt/wt before blending.

Solutions of 0–25% starch were measured, with or without 3% salt. Next, concentrations of 0 to 15% salt were added to water or 20% starch solutions and measured. Solutions of 21% starch were blended and measurements were taken at 1 min intervals. After 15 min of measurement, the solutions were again blended for 5 min in a Waring Blender, and dielectric properties were again measured. In one experiment, 100 µL \( \alpha \)-amylase (A 6380 type-II; from bacillus species, Sigma, San Francisco CA) was added to 20g of the 20% starch solutions at 25°C. The \( \alpha \)-amylase solution had been prepared by dissolving 25 mg enzyme in 1 mL of Tris buffer at pH 7.

An open ended coaxial probe and network analyzer were used to measure dielectric properties (85070B and 8752C, Hewlett-Packard Company, Denver, CO). The probe was mounted with the ground-plane flange facing up. An o-ring sealed the probe into a hole in the bottom of a 2.5 cm diameter stainless steel sample holder. The probe and cable were fixed so they could not be moved during sample measurement. A calibration was done using a short, air and water, before each set of experiments, then checked to insure the calibration was stable. The dielectric properties were automatically calculated from the phase and amplitude of the reflected signal by the computer. All measurements were made at 2450 MHz and 25°C. The average of three measurements was reported. All measurements were reproducible ±6%.

Viscosities were measured with the Contraves rheomat (115, Rheometric Scientific, Piscataway, NJ). Measurements were taken at 15 shear rates and the shear rate plotted vs the shear stress to determine the consistency index which was derived from the power law equation:

\[
\tau = K\dot{\gamma}^{n}
\]

where \( \tau \) is the shear stress (Pa), \( K \) is the consistency index (Pa·s\(^n\)), \( \gamma \) is shear rate (s\(^{-1}\)), and \( n \) is the flow behavior index.

Statistics were performed using the two sample t-test assuming equal variances. Sample differences were defined as significant when the two-tailed p value was <0.001.

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RESULTS & DISCUSSION

The dielectric properties were measured for various concentrations of starch in solution, with and without 3% salt (Fig. 1). The decrease in the dielectric constant due to salt addition, and the corresponding increase in dielectric loss factor was evident. Addition of salt to food systems with a high water content is known to decrease the dielectric constant and increase the dielectric loss. As discussed by Mudgett (1985), addition of salt to water has two important influences on dielectric properties. First, addition of dissolved ions binds water molecules. The degree of binding is directly related to the nuclear charge effect that depends on the size and charge of dissolved ions. This causes a reduction in polarization of the water and a decrease in the dielectric constant. Second, the dielectric loss factor is elevated above that of pure water because of the electrophoretic migration of dissolved salt, which is also directly related to the size and charge of the dissolved ions.

As the concentration of starch increased, the dielectric constant significantly decreased in both the samples with and without salt (Fig. 1). The samples with salt had an overall lower dielectric constant because water was bound by both the starch and the salt, but they followed the same trends as samples without salt. This decrease was caused by the binding of water molecules by starch. As the starch hydrates, it binds water, which decreases the polarization of the water and hence the dielectric constant. Similar results were reported by Padua (1993) using proton NMR.

The dielectric loss of starch solutions without salt did not change with starch concentration (Fig. 1). The dielectric loss was independent of concentration and not different from the value for pure water at starch concentrations up to 25%. Unlike the dielectric constant, the dielectric loss was not sensitive to minor changes in average mobility of water in a starch-water solution. Umbach et al. (1992) reported similar results for starch-gluten-water mixtures where increasing moisture contents affected the dielectric constant but not dielectric loss.

The dielectric loss for solutions containing salt decreased with increasing starch concentration, up to 25% starch (Fig. 1). Since the dielectric loss of the solutions without salt did not change with changing starch concentration, the observed change could not be due to changes in water mobility due to binding of water by starch (Fig. 1). Therefore we hypothesized that the decreasing dielectric loss resulted from a binding or interaction of the salt with the starch. If salt mobility were inhibited at increasing starch concentrations, the dielectric loss would decrease as shown. Starch may interfere with the electrophoretic migration of salt in response to the applied electromagnetic field through viscosity effects, or may directly bind the salt molecule.

In all of the samples, except for the dielectric loss value of the no salt sample, there was an abrupt decrease in all dielectric values at 10% starch. This corresponds to the concentration at which the samples become notably more viscous. Lower concentrations can be mixed by hand, but at >10% a blender must be used. This is also about the concentration at which the consistency index increased notably (Fig. 2).

The addition of salt to the starch solution increased its viscosity (Fig. 2). With increasing starch, the consistency index increased, as expected. The consistency index for the samples containing salt is higher than the corresponding samples without salt. Osman (1975) reported that the addition of salts to corn starch solutions caused an increase in viscosity that followed the lyotropic series of the anions. However, the addition of salt to a hydroxypropyl modified starch decreased granule swelling (Rutenberg and Solar, 1984), which would be expected to decrease viscosity in contrast to observed results.

Concentrations of 0 to 15% salt were added to samples with 20% starch or with no starch (Fig. 3). If there were no interactions be-
between salt and starch it would be expected that the dielectric loss of the two solutions would be similar. Instead the dielectric loss of samples with starch was depressed in response to increasing salt. With increasing concentrations of salt, the dielectric loss values were lower than they would have been with no starch present, similar to Fig. 1 where dielectric loss values decreased with increasing starch.

Immediately after mixing, the dielectric properties were measured at 1 min intervals to determine how they changed over time. Results for all starch concentrations were similar, thus only data for 21% starch is shown (Fig. 4). When no salt was present, the measured dielectric constant and loss were unchanged over time, thus no further starch hydration was occurring. When salt was present, the dielectric loss for the starch solutions decreased with time to a constant value after about 5 min, while the dielectric constant continued to decrease with time. Values of both the dielectric constant and the loss factor decreased with time, from 1 to 10 min for samples with salt. The 1 min measurements for the dielectric constant of the samples with and without salt were not different.

After allowing the samples to hydrate for 20 min, the dielectric properties and consistency index were measured, then the sample was remixed and measured again. After reblending, the consistency index was lowered to almost half, in both samples with and without salt (Table 1). The dielectric constant increased after blending for both samples while the loss increased only when salt was present. The mechanical agitation may have disrupted the interactions between salt and starch, or the organization of the hydrated starch granules, reducing viscosity and increasing dielectric loss.

α-Amylase was added to the starch mixtures to convert the starch to glucose and limit dextrins. This was done to remove any interactions between salt and starch without changing composition, except to convert starch to glucose, and it also decreased the viscosity. The dielectric constant, with or without salt, increased with time, as amylase cleaved the starch (Fig. 5). The dielectric constant of 20% starch was 50 with 3% salt and 54 without. The dielectric constant of 20% sucrose was 63 with 3% salt and 70 without. Thus it would be expected that the dielectric constant for both solutions would increase as the starch was converted to sugars.

The dielectric loss did not change over time when no salt was present, but the dielectric loss increased when salt was present (Fig. 5). Thus, the starch to glucose conversion had no effect on the dielectric loss of the water or carbohydrate. When salt was present, the dielectric loss increased as hydrolysis proceeded, indicating the salt molecules became more mobile in response to the electromagnetic field. Apparently the starch–salt interaction was lost when starch was hydrolyzed.

The exact nature of the interaction between salt and starch is unclear. Chinachoti et al. (1991) used sodium-23 NMR to show that when starch gelatinized, the mobility of sodium ions decreased because of salt–starch interactions. Hydroxypropyl starches are typically considered less sensitive to ionic environments than other starches; however, salt is added to the starch during the modification process because it reduces granule swelling (Rutenberg, and Solarek, 1984). Modification of the starch occurs in an alkaline environment which may increase the binding of salt (Oosten, 1983). It is likely that the hydroxyl groups of starch reversibly bind sodium ions, sim-

![Fig. 4—Changes in the dielectric constant and loss over time for 21% starch, with and without addition of salt.](image)

![Table 1—Dielectric properties of 20% starch before and after blending](image)

<table>
<thead>
<tr>
<th>Consistency index</th>
<th>Dielectric constant</th>
<th>Dielectric loss factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially blending</td>
<td>After blending</td>
<td>Initially blending</td>
</tr>
<tr>
<td>no salt</td>
<td>66</td>
<td>39</td>
</tr>
<tr>
<td>3% salt</td>
<td>106</td>
<td>52</td>
</tr>
</tbody>
</table>

The consistency index shows the decrease in viscosity caused by the blending.

![Fig. 5—Effect of enzymatically induced changes on the dielectric constant and loss measured over time, with and without addition of salt. 100 µL α-amylase (25 mg/mL) added at time = 0 to aqueous solution of 20% starch.](image)
ilar to the binding action when sodium hydroxide is added (Oosten, 1983).

Since viscosity was also altered by salt addition, it is possible that changes in mobility reflected in the dielectric loss were due to viscosity effects. However, previous experiments have shown that large viscosity changes caused by the addition of gums had no effect on dielectric properties.

CONCLUSION

WHEN SALT IS ADDED TO A STARCH SOLUTION, THERE APPEARS to be an interaction that limits salt mobility in response to an electromagnetic field. This interaction lowers the dielectric loss factor, which may influence heating rate during microwave heating.

REFERENCES


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