Dielectric and Thermal Transition Properties of Chemically Modified Starches During Heating[1]

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ABSTRACT

The dielectric properties and swelling characteristics of chemically modified starches with differing degrees of substitution and at different starch-to-water ratios were evaluated before and during heating. Thermal transitions and swelling properties of the starch granules were evaluated by differential scanning calorimetry (DSC) and microscopy, respectively. Dielectric constants (K′) of all starches remained constant during heating, and the loss factors (K″) and absorptivities (1/Ri) of most starches decreased slightly during heating except during starch thermal transition times as measured by DSC.

Chemically modified corn starches have a variety of applications in food and other industries. For example, during commercial preparation, food products are often subjected to prolonged heating and high shear stress. Starches are chemically modified to withstand these stresses. Some of the chemical modifications that are used change the hydrophilic-hydrophobic properties of the starch granules by adding ionic or polar charges or hydrophobic groups to the granules. These modifications could also change the response to microwave radiation through changes either in dielectric properties resulting from the introduction of the new chemical groups or in functional properties such as viscosity or temperatures of phase transitons.

Dielectric properties are defined in terms of dielectric constant (K′) and dielectric loss factor (K″), which in turn contribute to the absorptivity (1/Ri) of the system. K′ is a measure of the ability of a material to couple with microwave energy. In general, the more polar the molecule, the more it can couple and the higher K′. K″ is the measure of the ability of a material that is reorienting in a rapidly oscillating field to dissipate electrical energy as heat. The penetration depth is how far the microwave radiation enters the food before it is reduced to 1/e of the initial field strength. The absorptivity is the inverse of the penetration depth. Two factors that affect a molecule's dielectric properties are its charge and its environment. The dielectric properties of a system are also affected by the presence of water, both directly because of changes caused by the introduction of water into the system and indirectly by effects that occur as a consequence of the presence of water, such as changes in viscosity and/or starch phase transitions. The environment changes as heating occurs, and despite the widespread use of microwave heating, these properties have not been investigated systematically in food systems. Therefore, it is of interest to examine the consequences of introducing the various substituent groups into starch.

Microwave heating is greatly influenced by the presence of water in foods (von Hippel 1954, Mudgett 1982) Therefore, dry food components such as unmodified starch granules are thought to be electrically inert. However, they could affect the electrical properties as they change the hydration properties and viscosity of the system. Also, factors such as changes in heat capacity and thermal diffusivity can also affect the dissipation and retention of heat (Wei et al 1985a,b)

The procedures followed during chemical modification may alter starch granule stability or molecular bonds in such a way that either more or less energy is required to disrupt starch granule order. For this reason, thermal analysis of the different starch types could give some useful information relating to starch structure.

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The objectives of this research were to evaluate the effects of different functional groups on the microwave-absorbing properties, thermal transitions, and swelling properties of aqueous dispersions of modified corn starches. The dielectric properties and starch thermal transition onset temperatures and enthalpies for waxy, normal, potato, and chemically modified tapioca and waxy and normal corn starches with differing degrees of substitution were measured at two starch-water ratios during heating. Video-enhanced microscopy was used to study the swelling properties of the starches at room temperature and during heating under dilute conditions.

MATERIALS AND METHODS

The following starches were supplied by National Starch and Chemical Co. (Bridgewater, NJ): waxy corn starch esterified or etherified with acetate (hydrophilic, polar), phosphate (hydrophilic, negative ionic charge), quaternary and tertiary ammonium (hydrophilic, positive ionic charge), hydroxypropyl (hydrophilic, polar), or octenylsuccinate (hydrophilic, negative ionic charge and hydrophobic group); normal corn starch etherified with hydroxypropyl (hydrophilic, polar); tapioca starch etherified with quaternary ammonium; unmodified potato starch, waxy corn starch, and normal corn starch. In addition, waxy and normal corn starches were modified with quaternary ammonium by using the method of Carr and Bagby (1981) in our laboratories. The degree of substitution (DS) for modifications of waxy corn starches were as follows: acetate 0.286 DS, phosphate 0.0087 DS, 0.026 DS; quaternary ammonium 0.036 DS, 0.052 DS, 0.074 DS; tertiary ammonium 0.035 DS, 0.053 DS; octenylsuccinate 0.015 DS; hydroxypropyl 0.055 DS, 0.085 DS, 0.133 DS. The DS for modifications of normal corn starches were as follows: hydroxypropyl 0.055 DS, 0.098 DS, 0.148 DS; quaternary ammonium 0.067 DS. The tapioca starch modified with quaternary ammonium had a DS of 0.033. The potato starch was unmodified, but if the phosphate naturally contained in this starch was calculated as a DS, it would be 0.003. The DS is defined as the average number of sites per glucose unit that possess substituent groups (Whistler and Daniel 1985); it was calculated according to the method of Wurzburg (1988). The DS for the commercially supplied starches modified with quaternary and tertiary ammonium analyzed and calculated by our laboratory were the same as those listed by the manufacturer. To remove any residual salts left from the derivatization process that might increase microwave coupling, all starches—whether derivatized or not—were washed five times in double-distilled deionized water and dried at room temperature. Final moisture contents were 7–10%.

Measurement of Dielectric Properties

The starches were mixed with double-distilled deionized water in a starch-water ratio of 1:1 or 1:2 (w/w) on a dry weight basis. An aliquot of starch and water was drawn into 10- or 20-μl pipettes

(Gold Seal Glassware, Clay Adams, Becton, Dickinson and Co., Parsippany, NJ) and inserted through a small hole in the center of the wave guide. The size of the pipette used depended on how absorptive the system was to the microwave radiation (i.e., the higher the absorptivity, the smaller the sample holder). The cavity perturbation method was used to determine the dielectric properties. A network analyzer (Hewlett Packard 8753A) equipped with a variable frequency, low-power microwave generator and a 12.2-cm wave guide was used to measure the K′, K″, and 1/Ri at 2450 MHz. The incident and transmitted frequencies were monitored through a frequency monitor (adapter model 5281A) The wave guide was placed inside a gravity oven (Stable-Therm, Blue Island, IL) and heated by conductive heat transfer from 30 to 90°C. Dielectric measurements were taken at 5°C intervals. The temperature was monitored inside the wave guide by using a fiber-optic temperature probe sensing system (Luxtron Fluoroptic Thermometer 1000A, Mountain View, CA). The procedure was replicated three times.

K′, K″, and 1/Ri were calculated by using the standard methods of testing for complex permittivity (ASTM 1976). A detailed description of these calculations and the cavity perturbation method can be found elsewhere (Brand 1987).

Thermal Transition Properties

Starch thermal transitions were obtained with a differential scanning calorimeter (Dupont model 910, Wilmington, DE) at a heating rate of 5°C/min. Dry starch (4.25 ± 0.425 mg) was weighed directly into previously weighed aluminum DSC pans. Water was added to obtain starch-water ratios of 1:1 and 1:2, and the total sample weight was determined after the pan was sealed. An empty aluminum DSC pan was used as reference. The method of Davis et al (1986) was used with the following additions: The samples were heated from 30 to 90°C, and the end temperatures were defined as the point at which the thermal transition peak returned to the baseline. Enthalpies were calculated as J/g for 1:2 starch-water ratio samples only. Three replications of the procedure were conducted for each starch, and means and standard deviations were calculated.

Microwave Heating Experiments

The temperatures of some starches in a 1:3 starch-water ratio were measured by using an experimental microwave oven built in our laboratory according to a method described by Zylema et al (1985) with the following exceptions: The oven was operated at an effective wattage level of 25 W (watts transmitted minus watts reflected), and temperatures were recorded at 20-sec intervals.

Video Microscopy

A Nikon Optiphot-Pol microscope fitted with rectified differential interference contrast optics and a Physitemp Peltier heating stage were used. A black and white television camera (Dage model NC68) with a Newvicon imaging tube was interfaced to this microscope by a Nikon 0.9-2.25X zoom lens. Dilute samples were prepared, and cover slips were sealed to the slides with optical adhesive (No. 81, Norland Products, Inc., New Brunswick, NJ) to prevent water loss during heating. The samples were viewed under normal light and polarized light during heating from 30 to 80°C at 5°C/min. The gelatinization range was defined as the difference between the temperature at which the first granule in the field started to swell and/or lost its birefringence and the temperature at which the last granule completely lost its birefringence and/or completed swelling.

RESULTS AND DISCUSSION

Dielectric Properties

The K′ of waxy and normal corn starches remained constant during heating (Fig. 1). However, K′ for both starches was higher for the samples with higher water ratios initially and during heating. The K″ of waxy and normal corn starches generally decreased as temperature increased, except that it was constant in the temperature range associated with starch thermal transitions as measured by DSC (62–75°C). Variations in 1/Ri data were similar to those observed for the K″ data since the K′ did not change over the temperature range used.

The dielectric behavior of waxy corn starches modified with octenylsuccinate (Fig. 2) was similar to that of the unmodified waxy corn starches during heating (Fig. 1). The dielectric constants remained constant during heating, and the K″ and 1/Ri generally decreased during heating, except that they were constant in the temperature range associated with starch thermal transitions as measured by DSC. The K′, K″, and 1/Ri of octenylsuccinate-modified waxy corn starches did not differ between the two starch-water ratios studied. Similar behavior was seen for acetate and hydroxypropyl-modified starches (data not shown). Also, at all levels of substitution, the dielectric properties of the hydroxypropyl-substituted waxy and normal corn starches were similar.

The K′ data for waxy corn starches substituted with quaternary ammonium (Fig. 3) and phosphate (Fig. 4) were similar to the data in Figure 1 and did not vary as the temperature was increased.

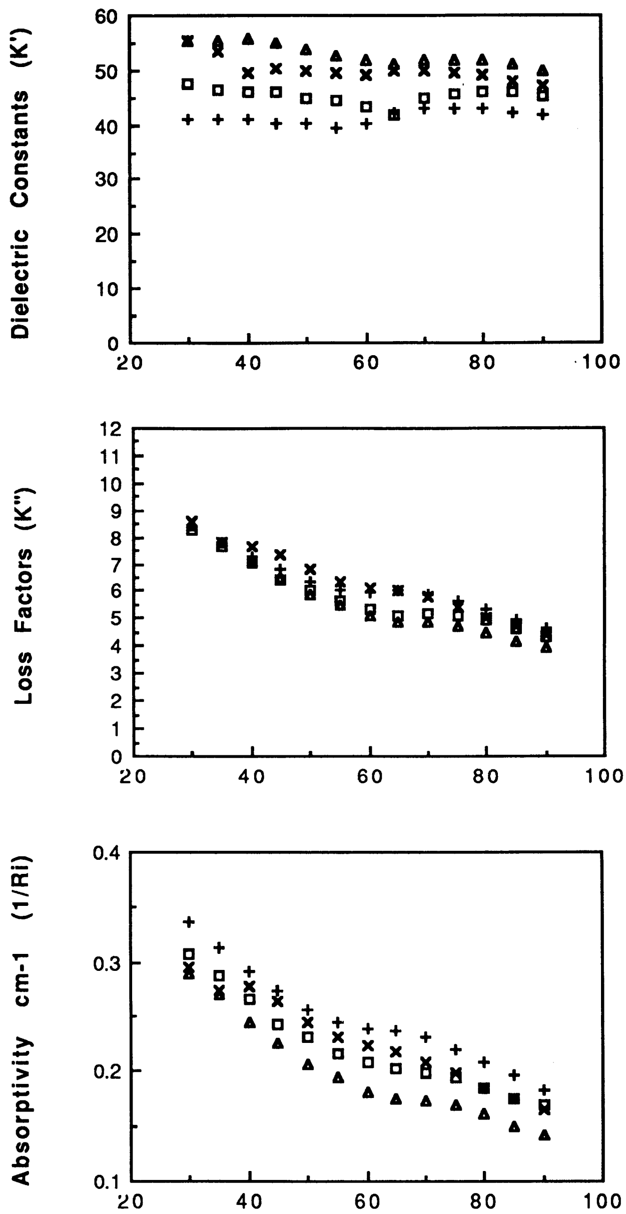

Fig. 1. Dielectric properties of mixtures of waxy and normal corn starches during heating. Ratios: □ = 1:1, △ = 1:2 waxy starch to water; + = 1:1, x = 1:2 normal starch to water.

However, in contrast to the results for unmodified starches and those modified with octenylsuccinate, acetate, and hydroxypropyl, K″ and 1/Ri for waxy corn starches substituted with quaternary ammonium and phosphate decreased initially, followed by increases in K″ and 1/Ri with increasing temperature during the temperature range associated with starch gelatinization. Then K″ and 1/Ri were relatively constant over the 60–90°C temperature range. Samples with a higher DS had greater values of K″ and 1/Ri than did those with a lower DS. The K′,K″, and 1/Ri of the 1:2 starch-water ratios for both of these modifications (data not shown) were the same as those of the 1:1 starch-water ratios. Both of these modifications added an ionic charge to the granule. Modifications done at a similar DS on a different starch source (tapioca) had similar values for K″ (data not shown), as did the tertiary ammonium modifications of waxy corn starch (data not shown). Since the residual salts left from the modification process were removed from all samples, the increase in K″ seemed due to the modification rather than to residual salts or starch source. The octenylsuccinate modification, which added an ionic charge

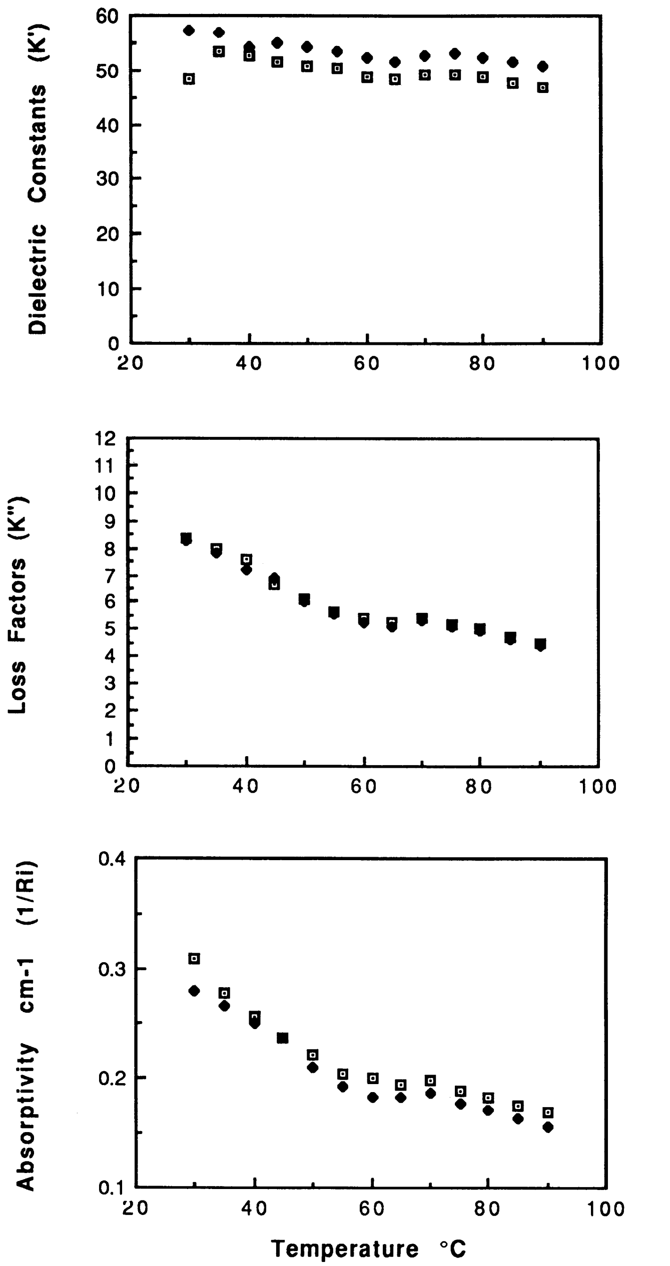

Fig. 2. Dielectric properties of mixtures of octenylsuccinate-substituted waxy corn starch and water during heating. Starch-to-water ratios: ▣ = 1:1, ◆ = 1:2.

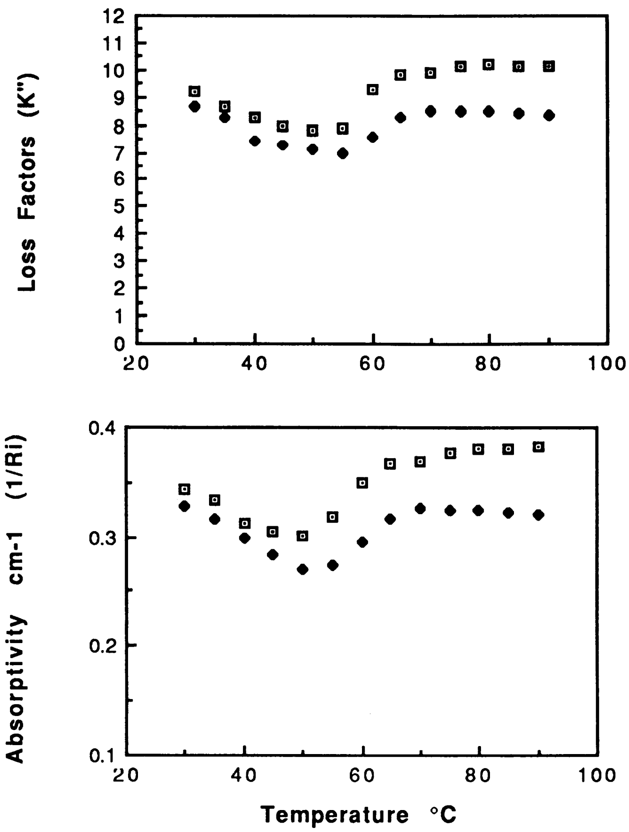

Fig. 3. Dielectric properties of starch-water mixtures (1:1) of commercially prepared waxy corn starches substituted with quaternary ammonium during heating. Degree of substitution: ▣ = 0.052, ◆ = 0.036.

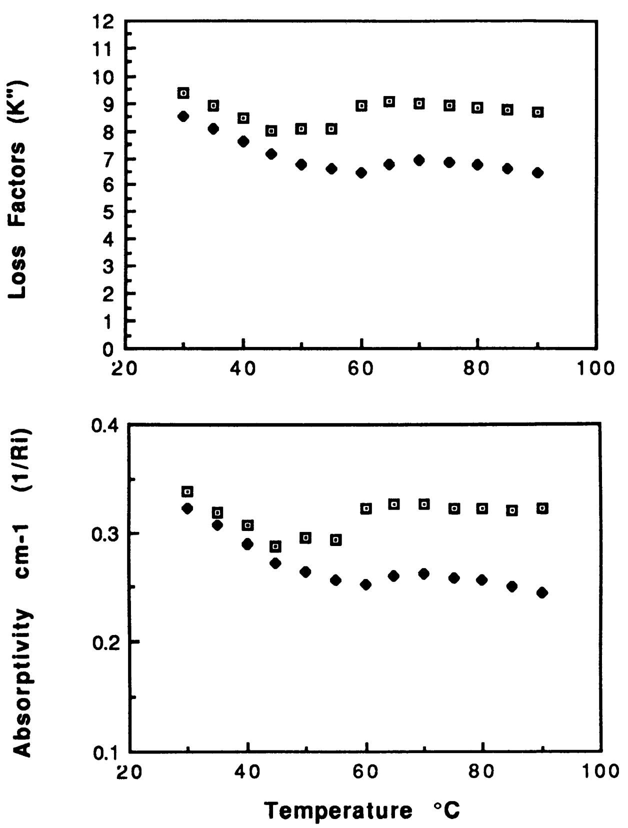

Fig. 4. Dielectric properties of starch-water mixtures (1:1) of phosphate-substituted waxy corn starches during heating. Degree of substitution: ▣ = 0.026, ◆ = 0.009.

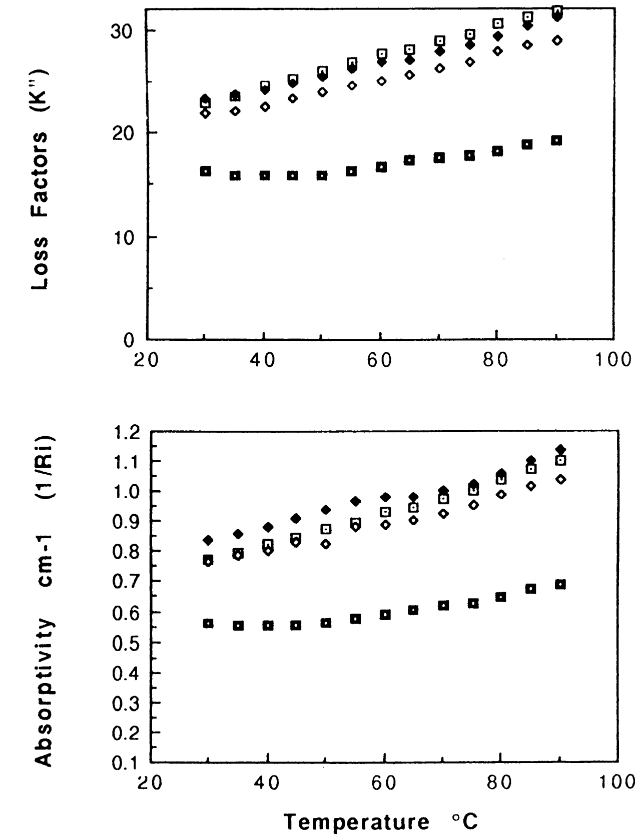

Fig. 5. Dielectric properties of mixtures of waxy and normal corn starches substituted with quaternary ammonium (prepared in our laboratory) during heating. Ratios: ⊡ = 1:1, ■ = 1:2 waxy starch to water; ◇ = 1:1, ◆ = 1:2 normal starch to water.

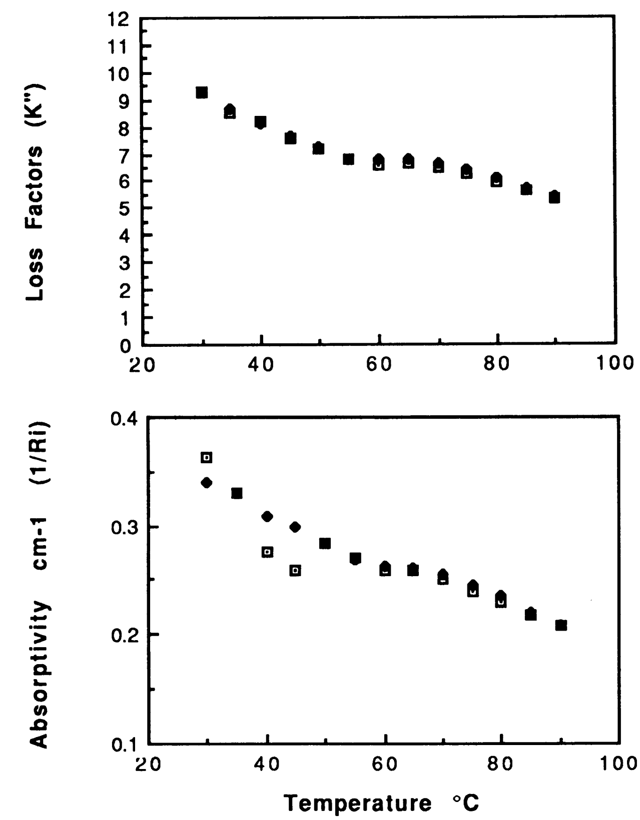

Fig. 6. Dielectric properties of mixtures of potato starches and water during heating. Starch-water ratios: ⊡ = 1:1, ◆ = 1:2.

and a hydrophobic group to the granule, did not show similar behavior (compare Fig. 2 with Figs. 3 and 4).

Figure 5 shows the K″ and 1/Ri values vs. temperature, respectively, for quaternary-ammonium-modified waxy and normal corn starches as prepared in our laboratory and which had the highest DS. The initial K″ and 1/Ri values for waxy and normal corn starches modified with quaternary ammonium were higher than those for pure water (10 and 0.25, respectively) and whey proteins (13–14 and 0.48–0.56, respectively), (Fleischmann 1991). Unlike other unmodified and modified starches, the K″ and 1/Ri values for 0.07-DS modified starches increased as the temperature increased. Whey proteins are thought to have higher dielectric properties than those of water because of the water-structuring effect of the protein (Kuntz 1975). The ionic modifications of the starch may have had a similar effect.

For chemically modified normal corn starch, K″ and 1/Ri values at the starch-water ratios studied were the same, as before. But for chemically modified waxy corn starch, the K″ and 1/Ri values were lower at the higher water ratio. The structures of waxy and normal corn starch granules differ. Although at a lower DS the samples did not show any difference in K″ and 1/Ri values, it is possible that these structural differences influence the dielectric behavior at higher DS. These structural differences were examined in later sections by using DSC and microscopy.

The modification process could have disrupted intermolecular and intramolecular hydrogen bonds that stabilize the granule structure. The starch modified with quaternary ammonium was slurried with the modifying agent at room temperature and high pH for 12 hr. Sodium sulfate salts are used to inhibit swelling, but to determine whether the modification process contributed to changes in the granule that could affect the dielectric behavior, waxy and normal corn starches were subjected to the same process used to modify starches with quaternary ammonium but without the modifying agent. The dielectric behavior of these samples (not shown) was the same as that of unmodified starches.

Potato starch naturally contains more phosphate than other starches. It is possible to compare the dielectric behavior of the naturally occurring phosphate with that of the chemically incorporated phosphate. The K″ and 1/Ri values of unmodified potato starches (Fig. 6) were slightly higher than those of unmodified corn starches (Fig. 1). Therefore, the behavior seemed due to the phosphate, whether modified or not.

These increases in dielectric properties result in a much shorter time to reach a particular temperature. For unmodified waxy corn starch and starches with similar dielectric behavior of several starches (Fig. 7), the temperature increased gradually during microwave heating. Just as the initial dielectric properties of most samples were similar, the temperatures before gelatinization were similar. After reaching the gelatinization temperature range, when the dielectric properties of some starches increased, the

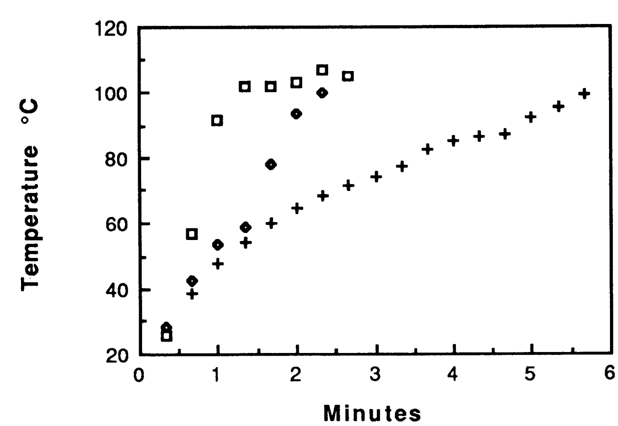

Fig. 7. Temperatures of unmodified and quaternary-ammonium-substituted starch-water mixtures (1:3) heated in an experimental microwave oven. □ = 0.07, ◆ = 0.05 degrees of substitution, + = unmodified starch.

temperature of these samples increased earlier. The laboratory-prepared sample with the highest DS had the highest initial dielectric values and the highest temperatures before gelatinization.

The molecular size and shape as well as the environment of the molecule influence K″, which is related to the resulting energy that can be released as frictional heat from the molecule as it returns to a relaxed position. The molecular physicochemical properties change as starch granules are heated. Thus, K″ will be influenced during heating as these events take place.

These results show that the dielectric properties of most modified starches were similar at starch-water ratios of 1:1 and 1:2. Waxy corn starches modified with quaternary-ammonium and phosphate with a higher DS had greater values of K″ and 1/Ri than did those with a lower DS. Although water is a major contributor to the dielectric behavior of foods, it seems that at the water concentrations used in this study, the type of chemical modification more strongly influenced the dielectric behavior than did changing the starch-water ratios from 1:1 to 1:2. Another reason for differences in dielectric behavior of the variously substituted starches could be that the modifications or procedures used during modification resulted in granule swelling and weakened bonds, which required different hydration and thermal input for transformations. Both acid and alkali are often used during the chemical modification process. However, Wootton and Manatsathit (1984) found that hydroxypropyl-modified corn starch that had been subjected to derivatization conditions without the derivatizing agent being present had the same onset temperature and enthalpy as did untreated starch. Under the right conditions, such as the presence of acids, the amorphous regions of the granule (Kartha and Srivastava 1985) can be disrupted, whereas alkali can cause the starch granules to swell even at low temperatures (Schirmer et al 1986, Wootton and Ho 1989). Above pH 7.5, the hydroxide ions could weaken the intermolecular and intramolecular hydrogen bonds, resulting in greater water absorption and lowering of the thermal transition temperature. At even higher pH, the granule integrity can be affected if starch chains are hydrolyzed by the hydroxide ions. Wootton and Ho (1989) found that despite extensive granule swelling, some birefringence was retained in wheat starch granules subjected to these conditions. This could indicate differences in the mechanisms of alkali or heat initiated thermal transitions.

The modification process for two of the starches used in the present study involved pH values above 7.5. Starches substituted with hydroxypropyl and quaternary ammonium were modified at pH 11.5 and 40°C. However, the dielectric properties of the two starches were not the same. The dielectric properties of hydroxypropyl starches were similar to those of unmodified starches. This supports the hypothesis that the type of modification contributed more to the change in dielectric properties than did the modification process itself. Furthermore, the processes used to produce starched modified with phosphate and quaternary ammonium are different, yet their dielectric behaviors were similar. Phosphate-substituted starches and unmodified potato starch, which had a phosphorus content equivalent to a DS of 0.003, had dielectric behavior that was different when compared with data from unmodified and most modified starches.

Thermal Transition Properties

To determine whether some of the differences seen in the dielectric properties might be reflected by change in the way starch swelled or gelatinized, the thermal behavior of starches was evaluated by DSC (Figs. 8 and 9). Table I contains the onset temperatures and enthalpies for the starches. (Enthalpies could

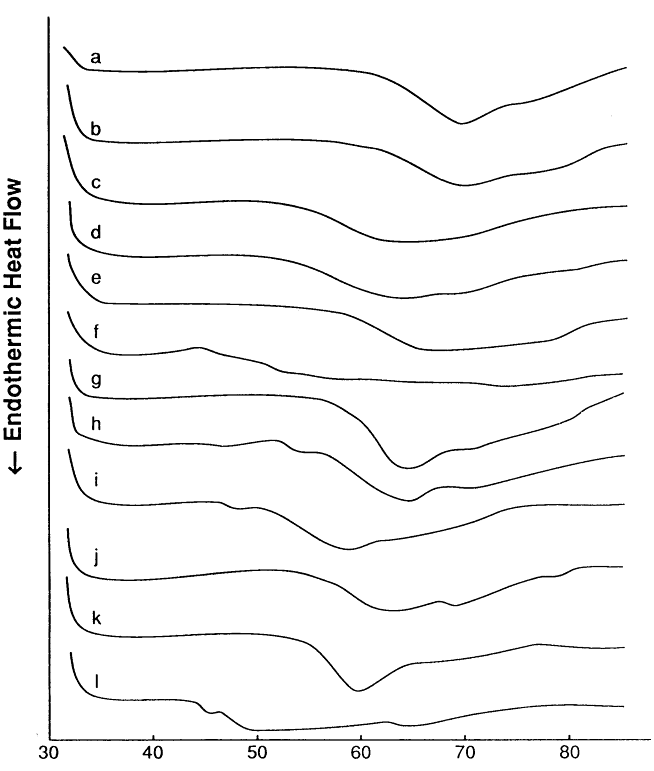

Fig. 8. Differential scanning calorimetric thermograms of starch-water mixtures (1:1) of the following: a, unmodified waxy corn starch; waxy corn starches modified with: b, octenylsuccinate 0.015 degree of substitution (DS); c, quaternary ammonium 0.036 DS; d, quaternary ammonium 0.052 DS; e, phosphate 0.0087 DS; f, phosphate 0.026 DS; g, acetate 0.286 DS; h, hydroxypropyl 0.055 DS; and i, hydroxypropyl 0.133 DS; j, unmodified normal corn starch; k and l, normal corn starches modified with hydroxypropyl 0.055 DS and 0.148 DS, respectively.

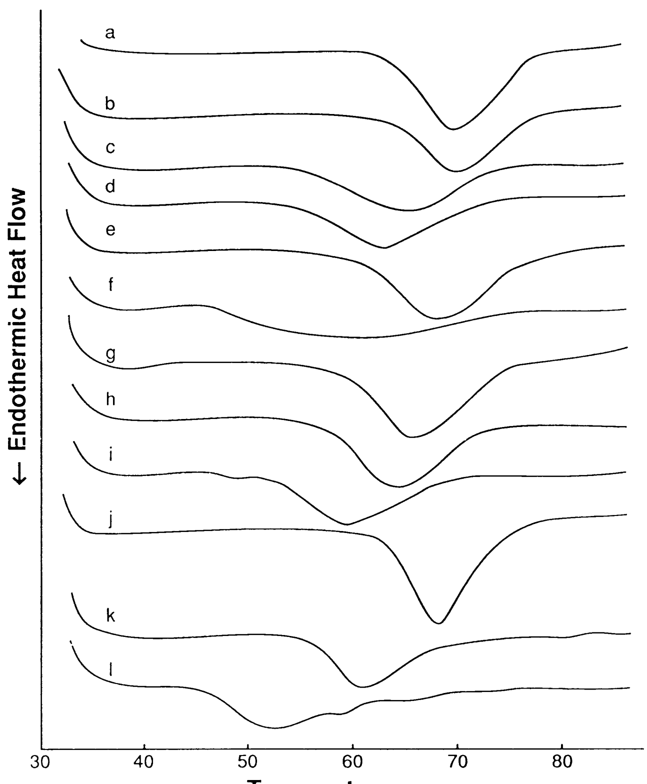

Fig. 9. Differential scanning calorimetric thermograms of 1:2 starch-water mixtures of the following: a, unmodified waxy corn starch; waxy corn starches modified with: b, octenylsuccinate 0.015 DS; c, quaternary ammonium 0.036 DS; d, quaternary ammonium 0.052 DS; e, phosphate 0.0087 DS; f, phosphate 0.026 DS; g, acetate 0.286 DS; h, hydroxypropyl 0.055 DS; and i, hydroxypropyl 0.133 DS; j, unmodified normal; k and l, normal corn starches modified with hydroxypropyl 0.055 DS and 0.148 DS, respectively.

not be calculated for the 1:1 starch-water mixtures because the endotherms were not sharp and/or had shoulders on the main peak.) At the 1:1 ratio, thermograms of unmodified starches and low DS modified starches generally showed the presence of a shoulder on the main endotherm, which is typical of a limited starch-water system. The starches showing this behavior were unmodified waxy starches and waxy starches modified with quaternary ammonium (0.052 DS), phosphate (0.0087 DS), acetate (0.286 DS), and hydroxypropyl (0.055 DS and 0.133 DS); and unmodified normal starches and normal starches modified with hydroxypropyl (0.055 DS and 0.148 DS). Other researchers have found that water concentration affects the sharpness of the thermal transition peak and temperature range of the thermal transition. In samples with limited water, such as those with a 1:1 starch-water ratio, the range is longer than for samples with a ratio greater than 1:1.5 (Collison and Chilton 1974, Donovan 1979, Burt and Russell 1983, Hoseney 1984, Chungcharoen and Lund 1987). It is possible that the type of chemical modification or the modification process opened up the granules in the higher DS samples and bonds were weakened, causing molecular changes to occur more easily in the limited water systems (as discussed earlier in the article) for the dielectric behavior of the starches.

At the 1:2 starch-water ratio shown in Figure 9, the endotherms were sharper than they were at the 1:1 starch-water ratio. The endotherm of waxy corn starch modified with octenylsuccinate was almost identical to that of unmodified corn starches. The endotherms of the waxy corn starches modified with quaternary ammonium at both DS were also similar to each other. The endotherms of the 0.055 DS waxy normal corn starches modified with hydroxypropyl showed differences in enthalpy even though the DS was the same for both starches.

In most cases, endotherms for all modified starches were not as sharp as those for the unmodified starches. The higher the DS, the more the endotherm was changed from that seen in unmodified starches. This was in contrast to the results for the dielectric properties, where small differences in K′ and K″ were seen as the starch-water ratios changed from 1:1 to 1:2. However, the thermal behavior as indicated by the onset temperature and enthalpy was affected by changes in starch-water ratios from 1:1 to 1:2.

Wootton and Manatsathit (1984) used DSC in studies of hydroxypropyl-substituted corn starches at starch-water ratios of 1:0.8–1:2 and found that modified starches had broader endotherms than did unmodified starches. The increases in molar substitution were accompanied by decreases in the enthalpy and onset temperatures of the thermal transition peak. They also found that at higher substitution levels, the endotherms obtained were too broad to permit measurement of the thermal transition. Starch that had been subjected to the derivatization conditions without the derivatizing agent had a higher enthalpy than did untreated starch. They attributed this to loss of damaged starch during the reaction and rinsing procedures used. Data from the current study indicated that two of the modified starches with low DS had higher enthalpies than did unmodified starches. The loss of damaged starch in the rinsing processes used could have contributed to this increase.

One can see from Table I that the onset temperatures for the two starch-water ratios were not different for unmodified waxy starch or for most of the modified starches, with the exception of unmodified normal corn starch. Generally, modified starches had lower onset temperatures than did the unmodified starches, with the exception of the octenylsuccinate-substituted starch at the 1:2 ratio and normal corn starch modified with hydroxypropyl (0.055 DS).

The phosphate-substituted starches had the lowest DS of all the modified starches. Phosphate-substituted starch (0.026 DS) had a low onset temperature and enthalpy. The onset temperatures of unmodified normal corn starch at 1:1 and 1:2 starch-water ratios differed, but the onset temperatures of modified normal corn starches were similar for both water concentrations.

In general, the enthalpies of some 1:2 starch-water mixtures of chemically modified waxy and normal starches were similar, or in some cases lower, than those of unmodified starches. A few of the modified starches had higher enthalpies than those of unmodified starches. This might be due to the modified starch source not being the same for all modifications.

Bulky chemical groups introduced into the molecular structure of the starch granule could contribute to a decrease in onset temperature of gelatinization. These groups could disrupt the intermolecular and intramolecular hydrogen bonds that stabilize the structure, or the hydrophilic groups added could increase the accessibility of the water to the starch. To see if a decrease

TABLE I
Thermal Behavior of Unmodified and Chemically Modified Corn Starches

Starch Type	Degree of Substitution	Onset Temperature (°C)[a] Starch-Water 1:1	Onset Temperature (°C)[a] Starch-Water 1:2	Enthalpy (J/g)[a,b] Starch-Water 1:2
Waxy	Unmodified	61.4 ± 0.42	62.1 ± 0.34	12.8 ± 0.11
Substitutions				
Octenylsuccinate	0.015	57.5 ± 0.40	61.6 ± 0.56	12.5 ± 0.04
Quaternary ammonium	0.036	51.3 ± 0.40	52.2 ± 0.48	14.0 ± 0.15
	0.052	51.5 ± 0.39	51.7 ± 0.19	13.3 ± 0.04
	0.074	48.3 ± 0.33	51.9 ± 0.84	9.4 ± 0.8
Phosphate	0.0087	57.4 ± 0.56	56.8 ± 0.35	14.3 ± 0.15
	0.026	47.4 ± 0.86	45.8 ± 1.05	10.7 ± 0.11
Acetate	0.286	55.9 ± 0.84	57.0 ± 0.11	12.9 ± 0.07
Hydroxypropyl	0.055	51.8 ± 0.78	53.5 ± 1.25	12.8 ± 0.12
	0.133	47.3 ± 0.72	50.9 ± 1.35	10.9 ± 0.06
Normal	Unmodified	52.9 ± 0.52	61.3 ± 0.65	11.6 ± 0.20
Substitutions				
Quaternary ammonium	0.067	52.8 ± 0.97	52.9 ± 0.14	6.6 ± 1.22
Hydroxypropyl	0.055	52.3 ± 0.54	522. ± 0.93	10.0 ± 0.13
	0.148	44.4 ± 0.23	44.1 ± 0.53	8.3 ± 0.08
Tapioca				
Substitutions				
Quaternary ammonium	0.033	51.4 ± 0.18	51.5 ± 0.56	14.8 ± 4.38
Potato starch	Unmodified	55.44 ± 0.53	55.64 ± 0.81	16.45 ± 4.03

[a]Plus or minus SD based on three replications.
[b]Enthalpies were not calculated for 1:1 starch-water ratio.

in the onset temperature of the starch thermal transition was related to changes in birefringence and swelling during heating, starch samples were examined during heating.

Video Microscopy

At room temperature, samples of modified starches were birefringent. The modified starches did not appear to differ in their structure from unmodified starches at this level of magnification. A 9°C gelatinization temperature range was seen for unmodified waxy granules, whereas a 16°C range was seen for granules modified with quaternary ammonium. For normal starch the gelatinization and swelling process was complete in 8°C. The hydroxypropyl-modified regular starches gelatinized in 12°C.

This supported results seen on DSC. The endotherms of modified starches were broader. As seen under the microscope, some of the granules lost their birefringence and swelled at earlier temperatures, whereas some gelatinized in the temperature range for unmodified starches. This behavior was seen in all modified starches and did not explain the difference in microwave absorption seen in some modifications.

If one compares dielectric behaviors of the starches with onset temperatures of the thermal transitions, modified starches with increased microwave absorption properties did not always differ from unmodified starches in thermal behavior. Therefore, dielectric behavior does not always relate to differences in thermal behavior. This is not surprising, since during microwave coupling the dielectric coupling properties can play a major role in how materials absorb microwave radiation (1/Ri). This does not need to affect molecular transformations as seen during heat input.

Earlier work on electron spin resonance of wheat starches showed that overall water mobility was not different for samples that were slurried and those that were not slurried, even though the starch granules were swollen, and the onset temperature and enthalpy decreased slightly as a result of slurrying (Pearce 1989). These results support our theory that dielectric behavior is due more to the nature of the substituent of these chemically modified starches as it influences dielectric properties than to the manner by which the substituent affects water mobility.

Johnson et al (1990) found a slight decrease in water mobility as measured by electron spin resonance in both unmodified and modified corn starches that were heated to 55°C. This decrease in mobility, although not much, could contribute to a decrease in loss factors seen in unmodified corn starches and some modified corn starches in the present work. It is not known whether starches modified with quaternary ammonium with the highest DS had different water-mobility patterns than did the unmodified and other modified starches.

Overall, these results are important in understanding the microwave heating of formulated foods. The results suggest that the level of absorptivity, both initially and during microwave irradiation, could be controlled by incorporating appropriate food-grade molecules that can tailor the heat transfer in variously formulated foods.

CONCLUSIONS

The K′ of modified and unmodified corn starches remained constant during heating. While the K′ of unmodified starches at the 1:2 starch-water ratios were higher than the K′ of unmodified starches at the 1:1 starch-water ratios, the K′ of modified corn starches were similar at both starch-water ratios. The K″ and 1/Ri for most starches generally decreased during heating. However, during the temperature range associated with starch thermal transitions as measured by DSC, these properties remained constant. The K′, K″, and 1/Ri of hydroxypropyl, acetate, and octenylsuccinate-modified starches were similar to the K′, K″, and 1/Ri of unmodified starches. The K″ and 1/Ri of modifications that added an ionic charge to the granule—quaternary ammonium, tertiary ammonium, and phosphate—either remained constant or increased during heating. In general, the enthalpies of 1:2 starch-water mixtures of chemically modified starches were similar to or lower than those of unmodified starches. The dielectric properties of most modified starches were similar at 1:1 and 1:2 starch-water ratios. Quaternary-ammonium-modified and phosphate-modified corn starches with a higher DS had greater values of K″ and 1/Ri than those with a lower DS. Although water is a major contributor to the dielectric behavior of foods, it appears that at the starch-water ratios used, chemical modifications that only added ionic charges to the starch molecules resulted in greater absorption of microwave radiation. The starch swelling and thermal transitions of all modified starches as seen by video-enhanced microscopy and DSC, respectively, occurred at lower temperatures than for unmodified starches, even though differences in microwave absorptivity were found only for three of the modified starches—quaternary ammonium, tertiary ammonium, and phosphate. This supports the view that the type of chemical modification more strongly influenced the dielectric behavior and was not necessarily related to the changes in the swelling of the modified starch granule shown by the lower onset temperatures of thermal transitions of all modified starches.

LITERATURE CITED

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1976. Standard methods of test for complex permittivity (dielectric constant and loss factor) of solid electrical insulating materials at microwave frequencies and temperatures to 1650°C. Part 39, D-2520-70. Pages 596-614 in: Annual Book of ASTM Standards. The Society: Philadelphia.

BRAND, B. A. 1987. Microwave-conventional heating of model cake systems containing components of different dielectric properties. Master's thesis. University of Minnesota, St. Paul.

BURT, D. J., and RUSSELL, P. L. 1983. Gelatinization of low water content wheat starch-water mixtures. Starch/Staerke 35:354.

CARR, M. E., and BAGBY, M. O. 1981. Preparation of cationic starch ether: A reaction efficiency study. Starch/Staerke 33:310.

CHUNGCHAROEN, A., and LUND, D. B. 1987. Influence of solutes and water on rice starch gelatinization. Cereal Chem. 64:240.

COLLISON, R., and CHILTON, W. G. 1974. Starch gelation as a function of water content. J. Food. Technol. 9:309.

DONOVAN, J. W. 1979. Phase transitions of the starch-water system. Biopolymers 18:263.

DAVIS, E. A., GRIDER, J., and GORDON, J. 1986. Microstructural evaluation of model starch systems containing different types of oils. Cereal Chem. 63:427-430.

FLEISCHMANN, A. 1991. The dielectric properties of whey proteins and starch systems. Master's thesis. University of Minnesota, St. Paul.

HOSENEY, R. C. 1984. Differential scanning calorimetry of starch. J. Food Qual. 6:169.

JOHNSON, J. M., DAVIS, E. A., and GORDON, J. 1990. Interactions of starch and sugar water measured by electron spin resonance and differential scanning colorimetry. Cereal Chem. 67:286.

KARTHA, K. P. R., and SRIVASTAVA, H. C. 1985. Reaction of epichlorohydrin with carbohydrate polymers. Starch/Staerke 37:297.

KUNTZ, I. D. 1975. The physical properties of water associated with biomacromolecules. Pages 93-109 in: Water Relations of Foods. R. B. Duckworth, ed. Academic Press: London.

MUDGETT, R. E. 1982. Electrical properties of foods in microwave processing. Food Technol. 36:109.

PEARCE, L. E. 1989. Application of electron spin resonance techniques to model batter and dough systems. Ph.D. dissertation. University of Minnesota, Minneapolis.

SCHIRMER, M. A., TOLEDO, M. C. F., and REYES, F. G. R. 1986. Effect of food ingredients on the viscosity of phosphate monoester of corn starch. Starch/Staerke 38:124.

VON HIPPEL, A. R. 1954. Dielectrics and Waves. Wiley: New York.

WEI, C. K., DAVIS, H. T., DAVIS, E. A., and GORDON, J. 1985a. Heat and mass transfer in water-laden sandstone: Microwave heating. AIChE J. 31:842.

WEI, C. K., DAVIS, H. T., DAVIS, E. A., and GORDON, J. 1985b. Heat and mass transfer in water-laden sandstone: Convective heating. AIChE J. 31:1338.

WHISTLER, R. L., and DANIEL, J. R. 1985. Carbohydrates. Pages 69-137 in: Food Chemistry. O. R. Fennema, ed. Marcel Dekker: New York.

WOOTTON, M., and MANATSATHIT, A. 1984. The influence of molar

substitution on the gelatinization of hydroxypropyl maize starches. Starch/Staerke 36:207.
WOOTTON, M., and HO, P. 1989. Alkali gelatinization of wheat starch. Starch/Staerke 41:261.
WURZBURG, O. B. 1988. Introduction. Pages 3-16 in: Modified Starches: Properties and Uses. O. B. Wurzburg, ed. CRC Press: Boca Raton, FL.
ZYLEMA, B. J., GRIDER, J. A., GORDON, J., and DAVIS, E. A. 1985. Model wheat starch systems heated by microwave irradiation and conduction with equalized heating times. Cereal Chem. 62:447.

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