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Modification of maize starch by thermal processing in glacial acetic acid ☆

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Abstract

Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) methods were used to determine if corn starch–glacial acetic acid mixtures can be melted and thermally processed at reasonable temperatures. DSC studies showed that the melting temperature of dry starch was reduced from about 280 to 180°C in the presence of >30% acetic acid. Glass transition temperatures varied from 110 to 40°C at 15 and 45% acetic acid, respectively. XRD showed the loss of native starch crystallinity and the formation of V-type complexes. Addition of 10% water decreased the melting temperatures to 140–150°C while addition of a base (sodium acetate) had little effect. Some possible applications of processing starch in glacial acetic acid will be discussed. Published by Elsevier Science Ltd.

Keywords: Starch; Acetic acid; Calorimetry; X-ray diffraction

1. Introduction

Although water is the solvent most often used for starch, non-aqueous solvents have been used as processing aids or plasticizers in the preparation of starch films and as reaction media for the preparation of starch derivatives having high degrees of substitution (DS). In the former case, hydrophilic molecules such as polyglycols, amides and amines serve as non-volatile plasticizers for starch (Poutanen & Forssell, 1996; Shogren, 1993; Young, 1984). Water, by contrast, will evaporate from starch films leading to embrittlement (Shogren, 1992; Zobel, 1988a). van Soest, Bezemer, de Wit and Vliegenthart (1996) and Tomka (1990) have studied the effect of glycerol and other polyols on the depression of the melting point of starch. Polar solvents such as DMSO and pyridine have long been used to swell and increase starch reactivity and reagent solubility for the preparation of high DS starch derivatives such as esters (Jarowenko, 1986; Lower, 1996; Mullen & Pacsu, 1942; Tessler & Billmers, 1996). Unlike water, these solvents do not react with reagents used to derivatize starch, side reactions are minimized and high DS products are more easily prepared.

Recently, there has been renewed interest in intermediate (1–2) and high (3) DS starch acetates for applications such as hot melt adhesives (Billmers, Paul, Hatfield & Kauffman, 1994), biodegradable films and molded articles (Bloembergen & Narayan, 1995; Borchers et al., 1993), foams (Altieri & Tessler, 1996; Shogren, 1996), coatings for paper and starch foam plates (Fringant, Rinaudo, Gontard, Guilbert & Derradji, 1998) and cigarette filters (Maheras, Hopkins & Tetziaff, 1994). Methods of preparation have included an aqueous suspension reaction using NaOH to neutralize all the acetic acid produced in the reaction (Billmers & Tessler, 1994) and suspension in acetic anhydride and acetic acid using catalytic amounts of H_2SO_4 (Lepeniotis & Feuer, 1997) or aqueous NaOH (Mark & Mehltretter, 1972; Shogren, 1996). The aqueous reaction is conducted near room temperature to prevent starch gelatinization while the non-aqueous ones are conducted at high temperatures. Little is known, however, about how acetic acid and small added amounts of water and catalyst affects the thermal transitions of starch as well as starch reactivity. Such information would be useful in understanding and predicting reactivity and rheology of starch–acetic acid/anhydride mixtures during continuous thermomechanical processing in an extruder, for example. A continuous, low volume process would be much more feasible than a large batch reaction due to the rapid, highly exothermic nature of the acetylation reaction at high temperatures.

☆ Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name USDA implies no approval of the product to the exclusion of other that may also be suitable.

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Table 1
Parameters derived from starch melting temperature data (T_m^o, melting temperature of the pure starch; ΔH, equilibrium heat of fusion; χ, polymer–solvent interaction parameter; errors are standard deviations in the parameter estimates from linear regression fit to Eq. (2))

Solvent	T_m^o (°C)	ΔH (kJ/mol)	χ
Acetic acid	286 ± 25	9.3 ± 2.1	0.94 ± 0.24
Water	286 ± 16	18 ± 2.0	0.64 ± 0.12

In this report, differential-scanning calorimetry was used to characterize the effect of acetic acid, water and sodium acetate on the melting and glass transitions of dry starch. X-ray powder diffraction, solid state NMR and size exclusion chromatography were used to characterize the effect of heating starch in the presence of acetic acid.

2. Experimental

2.1. Materials

Corn starch was Buffalo 3401 from CPC International, Englewood Cliffs, NJ and was vacuum dried at 110°C prior to use. Glacial acetic acid and sodium acetate were reagent grade and were obtained from EM Science and Aldrich, respectively.

2.2. Methods

2.2.1. Differential scanning calorimetry

Dry corn starch (5–9 g) and glacial acetic acid (15–60% based on total weight) or mixtures of acetic acid, water and sodium acetate (see Table 2) were added to 25 ml flasks with ground glass joints and stirred for 1 min. with a spatula.

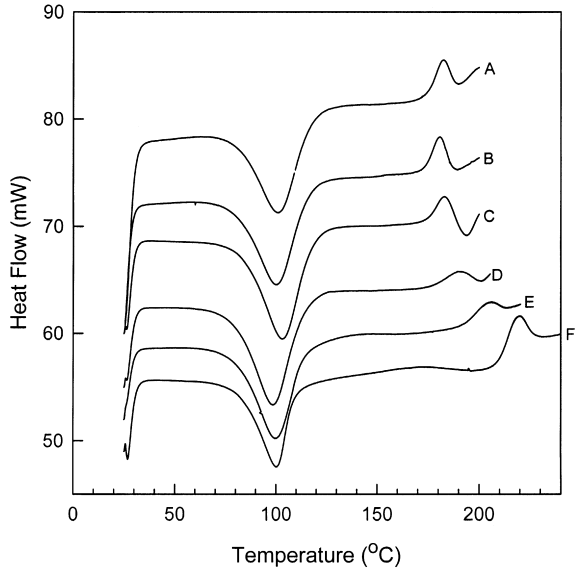

Fig. 1. Differential scanning calorimetry (DSC) first heating scans for dry starch in glacial acetic acid (GAA). Compositions in wt% of GAA: 60% (A), 45% (B), 30% (C), 25% (D), 20% (E) and 15% (F).

The flasks were then sealed with a ground glass stopper, wrapped with parafilm and left to equilibrate overnight. Portions (25–35 mg) of samples from the above flasks were transferred to stainless steel high-pressure DSC pans (Perkin–Elmer, Norwalk, CT) and quickly sealed. Pans were then heated in a Perkin–Elmer DSC7 from 25 to 180–230°C (above T_m, see Fig. 1) at 10°C/min to determine the melting temperature (T_m) and then cooled to 5°C and rescanned to measure the glass transition temperature (T_g). T_m and T_g were calculated using DSC7 software. Data presented are the average of 2–3 DSC runs. Average standard deviation of T_m measurement was 3°C.

2.2.2. Analytical methods

After heating, DSC pans were opened, the contents were removed and dried in a vacuum oven for 1 h at 50°C. Samples were then pulverised by shaking in a steel vial with a steel ball using a Wig-L-Bug Amalgamator (Crescent Mgr., Lyons, IL). The vial was cooled in liquid nitrogen prior to shaking.

X-ray powder diffraction analysis was performed with a Philips 1820 diffractometer operated at 40 kV, 30 mA with graphite filtered CuK_α radiation and a theta-compensating slit. Data were acquired in 0.05° 2θ, 4 s steps.

CP/MAS C-13 NMR spectra were obtained using a Bruker MSL-300 instrument. Mix and recycle times were 2 ms and 5 s, respectively. Samples were spun in zirconia rotors at approximately 3500 Hz.

Size exclusion chromatography (SEC) experiments were conducted on a Waters 150CV + instrument, equipped with differential refractive index and single capillary viscometer detectors. The column set consisted of a KB-G guard column and OHpak SB-806HQ and SB-806MHQ analytical columns, all from Shodex. The temperature of the column bank was maintained at 70°C. Injection volumes of 200 μl were used, with run times of 70 min and concentrations of 1mg/ml. Distilled, deionized water was employed as both solvent and chromatographic mobile phase, at a flow rate of 0.5 ml/min. Sample dissolution consisted of diluting 50 mg of analyte to 50 ml in volumetric flasks, heating to 80–90°C, while stirring, for 0.5 h, and then allowing the samples to solvate, at room temperature, for 2 days.

Column calibration was performed using pullulan narrow standards (Polymer Laboratories), and applying the concept of universal calibration (Grubisic, Rempp & Benoit, 1967). By measuring the refractive index and viscosity versus elution volume for starch, the resultant calibration curve for starch was obtained:

$$\log MW = 120 - 8.69RT + 0.226(RT)^2 - 0.00200(RT)^3 \quad (1)$$

where RT is retention time. The calibration curve was linear as a logarithmic function of the product of intrinsic viscosity times molecular weight (i.e. hydrodynamic volume) versus retention time using a third-order fit.

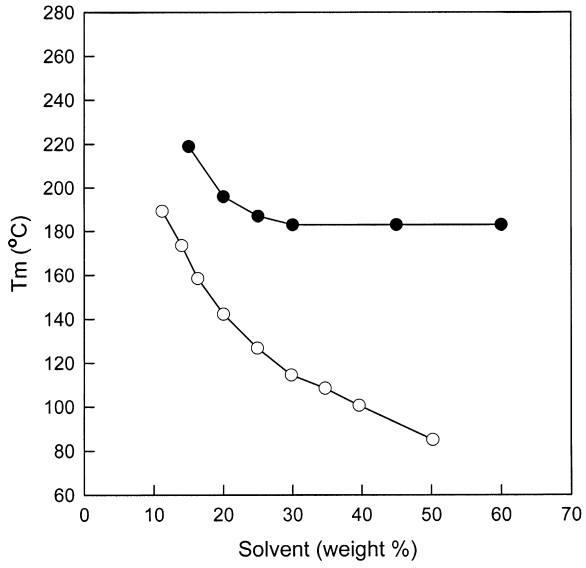

Fig. 2. Effect of glacial acetic acid (●) and water (○) on the melting temperature of starch.

Viscometer signal-to-noise (S/N) ratios were rather low for samples referred to in Fig. 8, so (refractive index) detector traces are presented.

3. Results and discussion

DSC heating curves for dry cornstarch in 15–60% glacial acetic acid are shown in Fig. 1. Large exotherms occur at about 100°C for all concentrations of acetic acid. The origin of these exotherms is not known but may be due to ordering of acetic acid molecules as they begin to swell and interact with starch molecules. No exotherms were found for samples containing 10% water (data not shown). Endotherms which reflect the melting of the crystalline portion of amylopectin (see X-ray diffraction data, Fig. 6) can be seen in each curve. The peak melting temperatures (T_m) are plotted versus weight percent of acetic acid in Fig. 2 and decline from about 220°C at 15% acetic acid to 180°C at >30% acetic acid. In contrast, T_m for starch in water (data from Shogren, 1992) declines continuously with increasing water content, reaching 90°C at 50% water (Fig. 2).

The second DSC heating scans for starch in acetic acid are shown in Fig. 3. Glass transition temperatures (T_g), obtained from these scans, are shown in Fig. 4. Values of T_g for starch in acetic acid decline from 110°C at 15% acetic acid to 40°C at 60% acetic acid. T_gs for starch in water (Shogren, 1992) decrease more rapidly as water content increases, reaching 20°C at 23% water.

Using lattice theory, Flory (1953) derived the following equation for the melting temperature depression of solvent swollen polymers,

$$1/T_m - 1/T_m^o = RV_2/\Delta HV_1(\nu_1 - \chi\nu_1^2) \quad (2)$$

where T_m^o is the melting temperature of the pure polymer, V_2 and V_1 are the molar volumes of the polymer repeat unit and solvent, respectively, ν_1 is the volume fraction of solvent, ΔH is the equilibrium heat of fusion and χ is the polymer–solvent interaction parameter. V was calculated by:

$$V = M/\rho \quad (3)$$

where ρ is density (1.5 was used for starch, French, 1984) and M is the molecular weight of a glucose residue or solvent. ν_1 was calculated by:

$$\nu_1 = (w_1/\rho_1)/(w_1/\rho_1 + w_2/\rho_2) \quad (4)$$

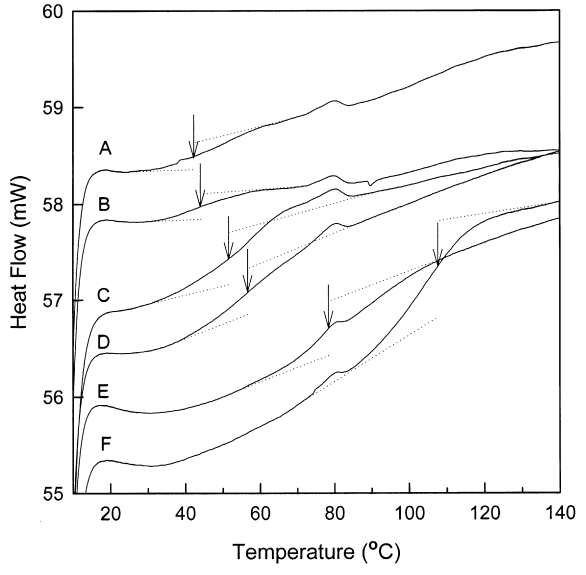

Fig. 3. Second DSC heating scans for dry starch in glacial acetic acid (GAA). Compositions in wt% of GAA: 60% (A), 45% (B), 30% (C), 25% (D), 20% (E) and 15% (F). Arrows indicate positions of glass transition temperatures. Dotted lines are baselines used for T_g calculation.

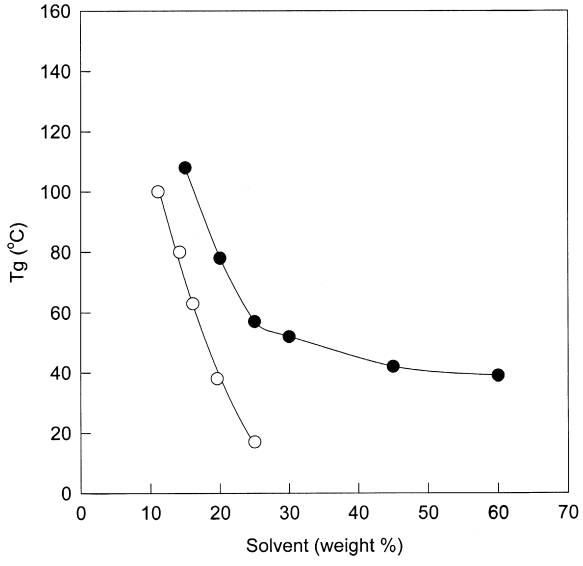

Fig. 4. Effect of glacial acetic acid (●) and water (○) on the glass transition temperature of starch.

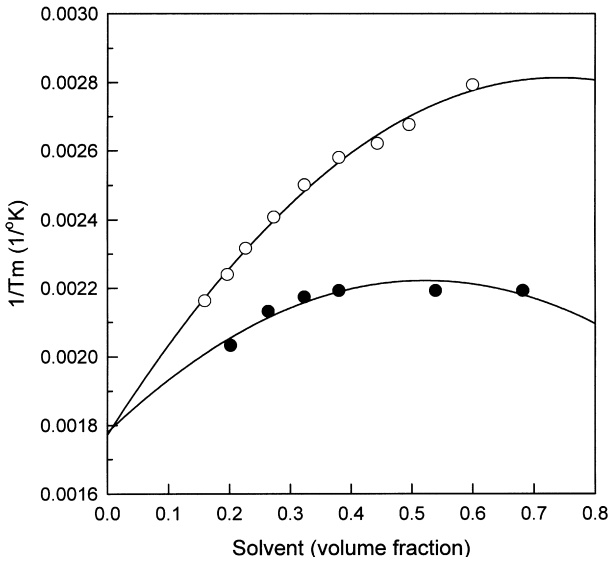

Fig. 5. Plots of the reciprocal of melting temperature versus volume fraction of solvent for glacial acetic acid (●) and water (○). Solid lines are fits of data to Eq. (2).

where w_1 and w_2 are the weight fractions of solvent and starch, respectively.

Using linear regression to fit $1/T_m$ to a quadratic function of ν_1 as in Eq. (2), one can calculate T_m^o, ΔH and χ from the intercept, slope and curvature, respectively. These plots are shown in Fig. 5 and parameters calculated from the plots are given in Table 1. The melting temperatures of dry starch obtained using acetic acid and water as diluents were similar (286°C) as would be expected. This value is similar to estimates of the melting temperature for dry lentil, adzuki, smooth pea and rice starches (252–298°C) using DSC melting data and a fit to Eq. (2) (Farhat & Blanshard, 1997). These authors pointed out that previous estimates of T_m^o for various starches were probably smaller than the correct values because the second term of Eq. (2) was neglected in fitting the data. χ is larger for starch–acetic acid than starch–water reflecting the less energetically favorable interaction between starch and acetic acid. Since acetic acid is less polar than starch, the two would be expected to have limited miscibility. The observation that no further change in T_m occurs above about 30% acetic acid implies that about one acetic acid molecule per glucose residue interact. Additional acetic acid would then likely form a separate phase. The calculated value of χ for corn starch–water (0.64) is similar to values obtained previously for wheat starch of about 0.6 (Donovan, 1979; Lelievre, 1973), for rice, pea and lentil starches (0.45–0.55) (Farhat & Blanshard, 1997) and implies that water is also a rather poor solvent for starch. Although the applicability of the Flory–Huggins theory to the DSC data may not be rigorous because of the non-equilibrium nature of the relatively rapid heating rates and the fact that Eq. (2) cannot predict a flattening of T_m at high solvent contents, it is useful for comparing different starch–solvent systems. Takahashi and Yamada (1998) found similar results are obtained from the original Flory–Huggins theory and after extension to include the effects of branching, non-equilibrium heating and crystal interfacial energy.

DSC data for cornstarch mixtures with acetic acid, water and sodium acetate are shown in Table 2. Addition of just 10% water to starch–acetic acid mixtures reduces the melting temperature of starch–acetic acid from 180–220 to 140–150°C. The Flory–Huggins expression for the melting point depression of starch can be extended for the case of two solvents (Lelievre, 1976):

$$1/T_m - 1/T_m^o = RV_2/\Delta HV_1[\nu_1 + \nu_3/x_3 + \nu_1\nu_3(\chi_{13} - \chi_{12} - \chi_{23}/x_3) - \nu_1^2\chi_{12} - \nu_3^2\chi_{23}/x_3] \quad (5)$$

where subscripts 1, 2 and 3 refer to acetic acid, starch and water, respectively and $x_3 = V_3/V_1$. By fitting all the melting data to Eq. (5) using linear regression (SAS), one obtains the interaction parameters $\chi_{13} = 2.0 \pm 0.6$, $\chi_{12} = 0.98 \pm 0.15$, $\chi_{23} = 0.63 \pm 0.11$. The large value for χ_{13} indicates an unfavorable energy of water–acetic acid interaction compared to water–starch. This suggests that water interacts preferentially with the starch and thus explains why a small amount of added water causes a large decrease in T_m for starch–acetic acid–water mixtures.

Glass transition temperatures were not observed in

Table 2
DSC data for dry corn starch in acetic acid/water/sodium acetate mixtures

Acetic acid (%)	Water (%)	Sodium acetate (%)	1st Heat		2nd Heat	
			T_m (°C)	Melting enthalpy (J/g)	T_m (°C)	Melting enthalpy (J/g)
15	0	0	220	7	–	–
45	0	0	182	5	–	–
15	10	0	150	5	133	0.6
45	10	0	141	5	109	1.4
15	0	5	n.d.[a]		–	–
45	0	5	176	6	–	–
15	10	5	152	7	132	1.0
45	10	5	140	5	106	1.2

[a] Sodium acetate not completely solubilized in acetic acid.

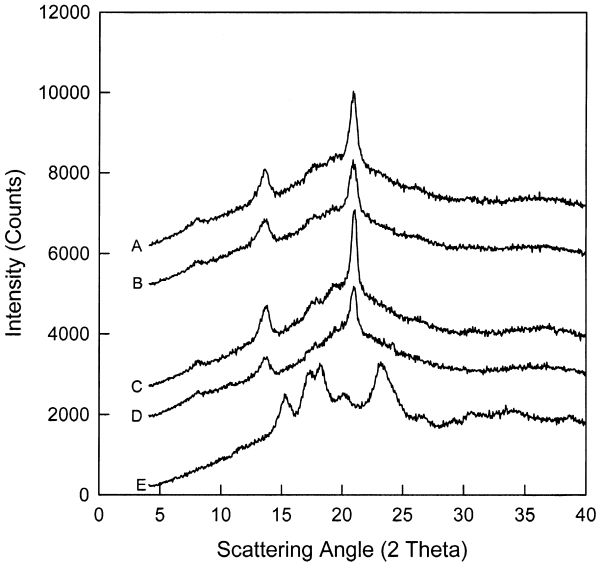

Fig. 6. X-ray powder diffraction scans of starch heated with 20% glacial acetic acid (GAA) (A), 45% GAA (B), 45% GAA + 10% water (C) and 45% GAA + 10% water + 5% sodium acetate (D). Native cornstarch (E) is shown for comparison.

mixtures containing 10% water (Table 2) probably since they were depressed below the starting temperature of the DSC scan (5°C). Melting endotherms in the range of 106–133°C were observed on second DSC heating scans and are probably due to the melting of amylose–acetic acid V-type complexes (see below). Interestingly, these were not observed in second heats of mixtures without water. Addition of sodium acetate resulted in small further decreases in the melting temperature of starch.

X-ray powder diffraction scans of starch heated with acetic acid, water and sodium acetate in the DSC are shown in Fig. 6. Peaks characteristic of the native A-type starch crystalline structure (Zobel, 1988b) have almost completely disappeared, confirming that the endotherms observed in the DSC scans are due to starch melting. All samples showed diffraction maxima at 7.8, 13.5 and 20.7° 2θ, lines characteristic of amylose V_a (anhydrous) complexes (Mikus, Hixon & Rundle, 1946; Takeo & Kuge, 1969). Previous work (Takeo, Tokumura & Kuge, 1973) also found that V-complexes were formed between amylose and acetic acid.

CP/MAS C-13 NMR spectra (Fig. 7) show that, even after drying in a vacuum oven for 1 h at 50°C, a starch–acetic acid sample still contained some acetic acid as evidenced by carboxyl and methyl carbon resonances at 174 and 21 ppm, respectively. The fact that these resonances are observable in a CP experiment implies that the acetic acid has been sufficiently restricted in mobility to allow H–C cross-polarization. Only small decreases in the intensity of these resonances were observed on further vacuum drying for 24 h at 110°C, suggesting the acetic acid is fairly strongly bound. Based on weights after drying and NMR peak areas, the bound acetic acid was estimated to amount to about 10% of the starch weight. Based on the upfield shift of the carboxyl carbon of the bound acetic acid (174 ppm)

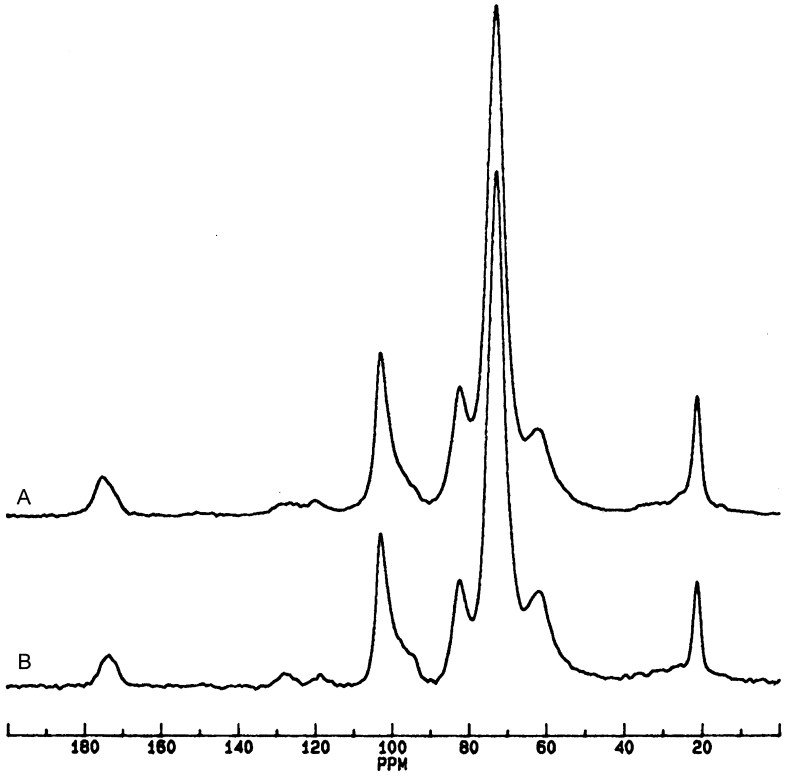

Fig. 7. CP/MAS C-13 NMR of starch heated with 20% glacial acetic acid to 215°C then dried in vacuo for 1 h at 50°C (A) or 24 h at 110°C (B).

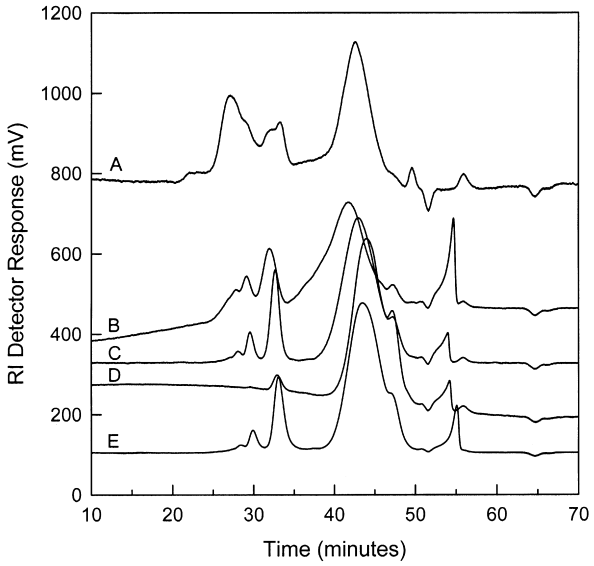

Fig. 8. SEC chromatograms of untreated starch (A) and starch after heating with 45% GAA + 10% water + 5% sodium acetate to 180°C (B), 45% GAA + 10% water to 180°C (C), 45% GAA to 200°C (D) and 20% GAA to 215°C (E).

from free acetic acid (177.3 ppm, Atta-ur-Rahman, 1986), it is likely that the acetic acid has been complexed inside the hydrophobic interior of the amylose helix (Gelb, Schwartz, Cardelino, Fuhrman, Johnson & Laufer, 1981; Shogren, Thompson, Greene, Gordon & Cote, 1991).

SEC chromatograms of unmodified starch and starch samples after heating in the presence of GAA, water and sodium acetate are shown in Fig. 8. The molecular weight distributions of all samples are quite broad, ranging from 10^4 to 10^9. There is considerable diminution of the higher molecular weight fractions of starch after heating in acetic acid, especially at higher temperatures. This may be due to hydrolysis of glycosidic linkages during the DSC heating. There is probably some water present even in the samples containing dry starch and GAA since starch will typically absorb a few tenths of a percent of water from air during the short time it is weighed and transferred. Some degradation may also have occurred during the heating required to dissolve the samples for SEC since pH values for samples containing acetic acid were 3.2–4.0. The decreases in molecular weight observed are, however, probably not sufficient to significantly change the melting temperatures of the starch since molecular weights are still much larger than the size of the linear branches of amylopectin involved in crystallization (MW ~ 3000).

The above demonstration that dry cornstarch can be gelatinized in glacial acetic acid has some useful implications for the preparation of starch derivatives. It would be expected that the reactivity of starch toward reagents such as anhydrides would be considerably enhanced after melting of starch in acetic acid. Synthetic reactions catalyzed by the reverse action of hydrolytic enzymes such as lipases or amylases may also be possible. It is well known that polysaccharides are much more reactive after first swelling and, particularly, solubilization or melting in a suitable solvent. Crystalline and highly hydrogen-bonded domains react slowly since access of the reagent is poor and mobility is low. Acetic acid has the advantages of being relatively safe and environmentally friendly and unreactive with most commonly used reagents for modifying starch. Experiments are currently underway to determine the reactivity of starch melted in acetic acid with several anhydrides and to further assess the changes in molecular weight occurring during the melting.

4. Summary

In summary, starch can be gelatinized (melted) in acetic acid in the absence of water by heating to >180°C. This is higher than the melting temperature of starch in water due to the larger molar volume of acetic acid (57 cm^3/mol) compared to water (18 cm^3/mol) as well as the unfavorable interaction energy of starch with acetic acid ($\chi_{12} = 0.98$) compared to starch and water ($\chi_{23} = 0.63$). Addition of 10% water further decreased the melting temperature to 140–150°C while addition of sodium acetate caused smaller decreases. The large value for the acetic acid–water interaction parameter ($\chi_{13} = 2.0$) suggests that water interacts preferentially with starch as opposed to acetic acid. X-ray diffraction scans of starch heated in acetic acid showed the loss of the native A-pattern and the formation of the V_a pattern typical of inclusion complexes. This was confirmed by solid state NMR experiments that showed the presence of methyl and carboxyl resonances and shifts in the carboxyl resonance commonly seen for complexed molecules. Some degradation of starch was noted after heating with acetic acid, especially at higher temperatures (>200°C).

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