ELSEVIER

Polymer 41 (2000) 2249–2263

polymer

A study of the molecular relaxations in solid starch using dielectric spectroscopy

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Received 26 November 1998; received in revised form 15 April 1999; accepted 20 May 1999

Abstract

A number of relaxations have been observed via dielectric spectroscopy, and possible molecular origins assigned, in a range of gelatinised and granular solid starches. At low temperatures (in the region of −120°C) two relaxations occur. The evidence indicated that these were due to small motions of the chain backbone and rotation of methylol groups (with the latter process activated at lower temperatures than the former). Around ambient temperature a relaxation proposed to be the glass transition was observed and, in granular starch only, gelatinisation caused a relaxation around 60–80°C. No major differences were discernible between different starch types. The water content was the most important influence on the position of the relaxations, since water acted as a plasticiser.

Keywords: Dielectric spectroscopy; Molecular relaxations; Polysaccharides

1. Introduction

Starch is a natural polymer system laid down in plants in the form of insoluble granules, the exact size and shape of which differ with biological origin. It consists mainly of two polymers, shown in Fig. 1; a poly(1-4)-α-D-glucan, amylose, which is essentially linear, and amylopectin, which is branched and consists of linear (1-4)-α-D-glucan chains connected through (1-6)-α linkages. The amylopectin component determines the bulk structure of the starch granule and is responsible for the crystalline component in them. Two crystalline unit cells, designated 'A' type and 'B' type, exist, depending on the biological origin of the starch ('A' type generally occurring in cereal starches and 'B' type occurring in tuber starches) [1].

Previous mechanical and dielectric studies of polysaccharides [2–9] (using amylose, cellulose, dextran and pullulan) have revealed relaxations in three temperature regions: (a) at sub ambient temperatures, which have been attributed to secondary relaxations from either small-scale molecular motions or rotation of the methylol group (where present; see Fig. 1); (b) in the vicinity of room temperature, which have been assigned variously to the glass transition and to relaxations involving motion of bound water; and (c) at elevated temperatures, which have been assigned to water loss and chain stiffening. However, it is clear that an overall consensus has not been reached on the details of the molecular origins of all these relaxations. One of the problems lies in the structural complexity of polysaccharides. The glucose residues are linked (1-6)-α in dextran but (1-4)-α in amylose and cellulose, whereas pullulan and amylopectin contain both (1-4)-α and (1-6)-α linkages; it is possible that these differences may affect the molecular relaxations. There is also a high degree of inter- and intra-molecular interaction, owing to the polar nature of the bonds in the glucose residues. Another problem lies in the sensitivity of polysaccharides to moisture, and the possibility that the molecular relaxations are controlled by bound water.

In the experiment reported in this paper, a series of natural granular and gelatinised starches with different biological origins was studied, over a range of water content, to examine the influences of starch type (hence amylose:amylopectin ratio and crystalline unit cell), crystallinity (since crystalline polymers often possess relaxations specific to the crystalline regions [10]) and water content on the molecular relaxations. Dielectric measurement of the complex permittivity provides a convenient and effective method for the study of relaxations, owing to the large frequency range, which is accessible and the ease of sample preparation.

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PII: S0032-3861(99)00366-3

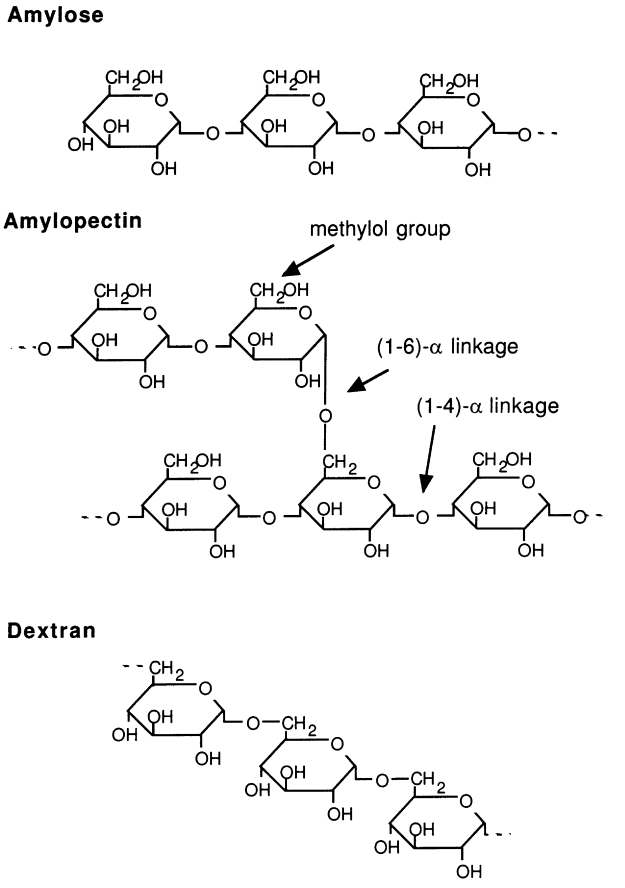


Fig. 1. Schematic diagrams of portions of the amylose and amylopectin molecules present in starch, and dextran.

2. Experimental

2.1. Materials and sample characterisation

Starch samples from different biological sources (amylomaize, maize, waxymaize, potato, wheat and rice) and dextran (from *Leuconostoc mesenteroides*) were purchased from Sigma–Aldrich Chemical Company. Table 1 displays the approximate amylose:amylopectin ratio and crystalline unit cell of each starch type [1,11]). Portions of each were stored in sealed boxes containing saturated solutions of certain salts which maintained the atmosphere within the boxes at chosen relative humidities at room temperature [12] (silica gel, humidity 0%; lithium chloride, 11%; calcium nitrate tetrahydrate, 50%; sodium chloride, 75%; potassium sulphate, 97%) for at least four weeks to ensure equilibration of the sample water content with that of the atmosphere (in this time the sample mass was found definitely to reach a constant value). Thermogravimetric analysis (Perkin Elmer TGA7) was used to assess the water content by heating a few milligrams of sample, immediately after removal from its constant humidity environment, from room temperature to 200°C at 10°C/min in nitrogen (flow rate 20 ml/min) and measuring the weight change. Differential scanning calorimetry (Perkin Elmer DSC7, equipped with a controlled cooling accessory connected to a liquid nitrogen supply) was used to identify the presence, or absence, of gelatinisation in heated 'wet' starch powders, for correlation with any dielectric relaxations.

Table 1
Approximate amylose:amylopectin ratios and crystalline unit cells in the different starch types studied [1,11]

Starch	Amylose:amylopectin ratio	Crystalline unit cell
Amylomaize	70:30	A
Maize (corn)	27:73	A
Potato	23:77	B
Wheat	27:73	A
Waxymaize	2:98	A

2.2. Dielectric spectroscopy

Measurement of the complex dielectric constant was effected by a Rheometrics Ltd. (formerly Polymer Laboratories) dielectric thermal analyser (DETA). Samples were mixed with a minimal amount of Dow Corning vacuum grease, sufficient to give a paste with no air pockets. The grease has a negligible dielectric response and is thermally stable in the temperature range from −140 to 200°C. The paste was placed between the two parallel metal plates in the DETA sample cell (diameter, 20 mm; separation, 0.5 mm). The vacuum grease ensured that the starch retained its water content at the level it possessed prior to mixing (the dielectric spectrum of a sample with a given water content tested immediately after removal from its constant humidity environment was identical to that from a sample from the same environment, mixed with grease and left exposed to the air for a week). Samples were heated from −140 to 200°C at a rate of 1°C/min; the slow heating rate was chosen to allow the sample as much chance as possible to thermally equilibrate during measurement of the complex dielectric constant. The dielectric response was measured at ten frequencies; 50 Hz, 100 Hz, 500 Hz, 1 kHz, 2.5 kHz, 5 kHz, 10 kHz, 25 kHz, 50 kHz and 100 kHz. Measurements were taken every 1.28 s, and four measurements at each frequency were averaged to give each data point; this corresponded on average to a resolution of one data point every 5°C per frequency during heating. Isothermal measurements were not taken due to the inability of the sample cell to satisfactorily maintain a constant temperature.

3. Results

3.1. Dielectric response: granular starch

Fig. 2 shows the plots of the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric constant as a function of ($1/T$) for granular waxymaize (amylopectin rich) and amylomaize (amylose rich) starch stored at 0, 75 and 97%

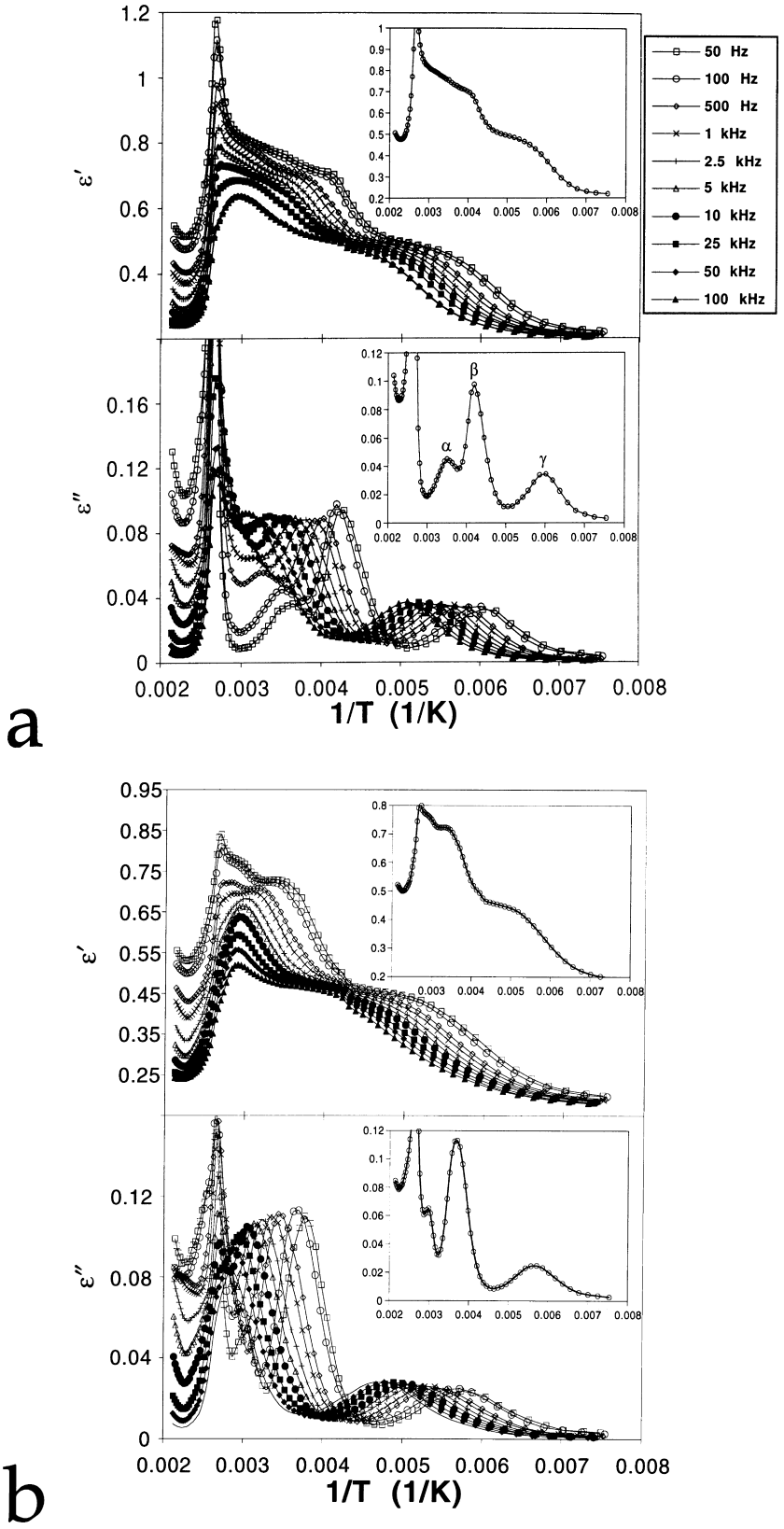
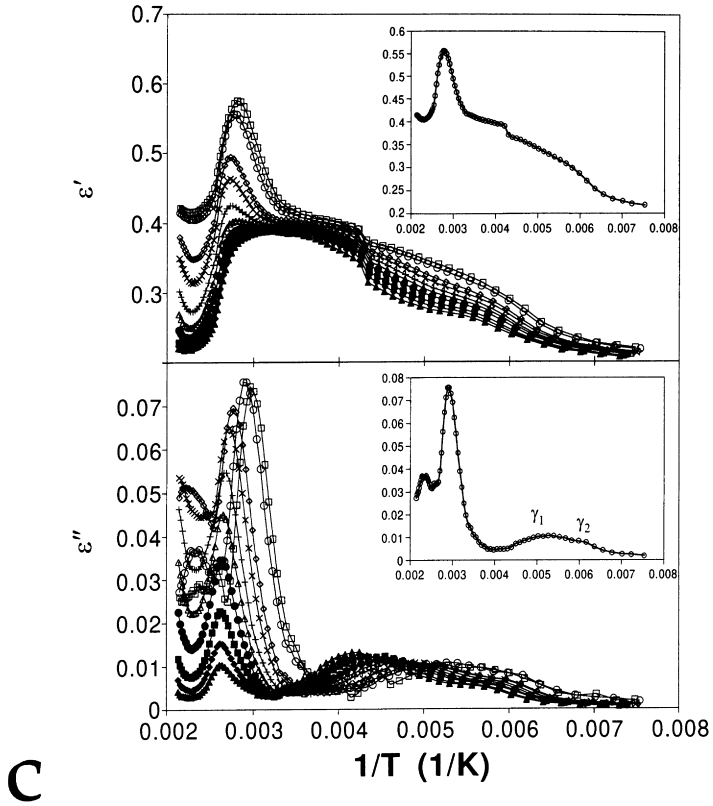


Fig. 2. Dielectric response of granular waxymaize starch stored at: (a) 97% humidity (water content 24.43 wt.%), (b) 75% humidity (water content 15.31 wt.%), (c) 0% humidity (water content 7.20 wt.%) and granular amylomaize stored at (d) 97% humidity (water content 24.45 wt.%), (e) 75% humidity (water content 16.23 wt.%) and (f) 0% humidity (water content 5.81 wt.%). The response at 100 Hz is shown inset to show the relaxation behaviour more clearly, while the main plots show the frequency dependence of the dielectric response (frequencies in all plots as marked for (a)).



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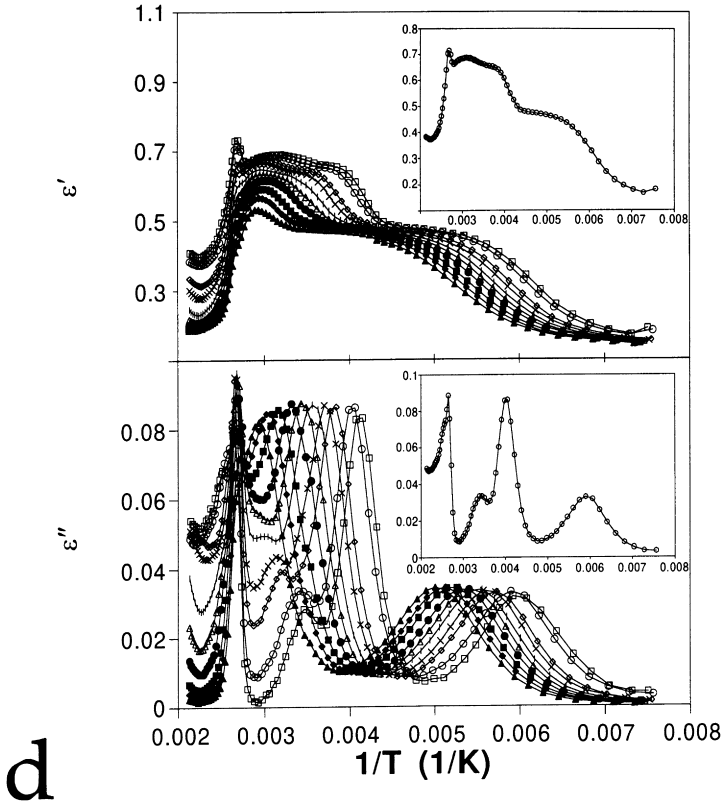

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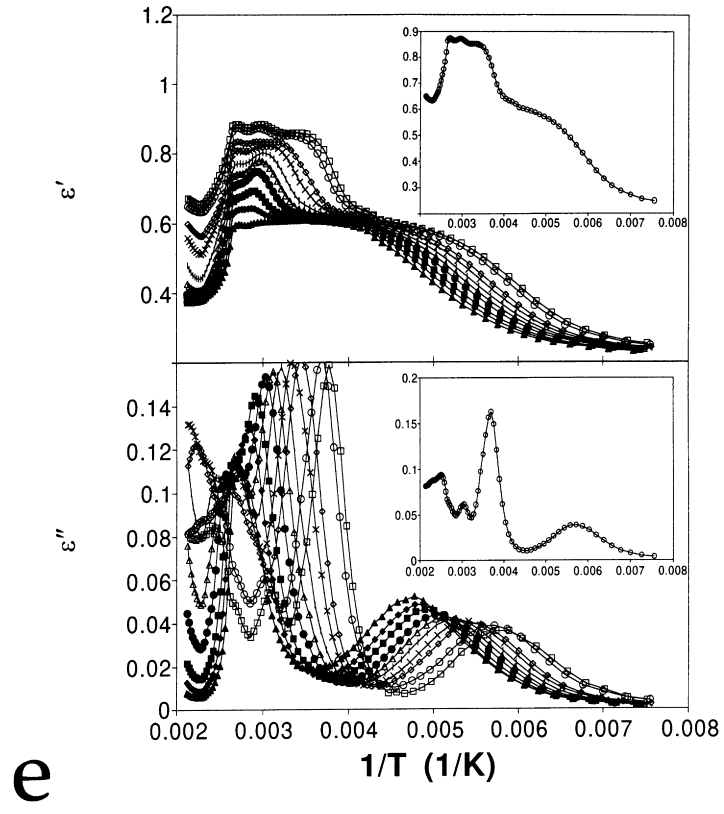

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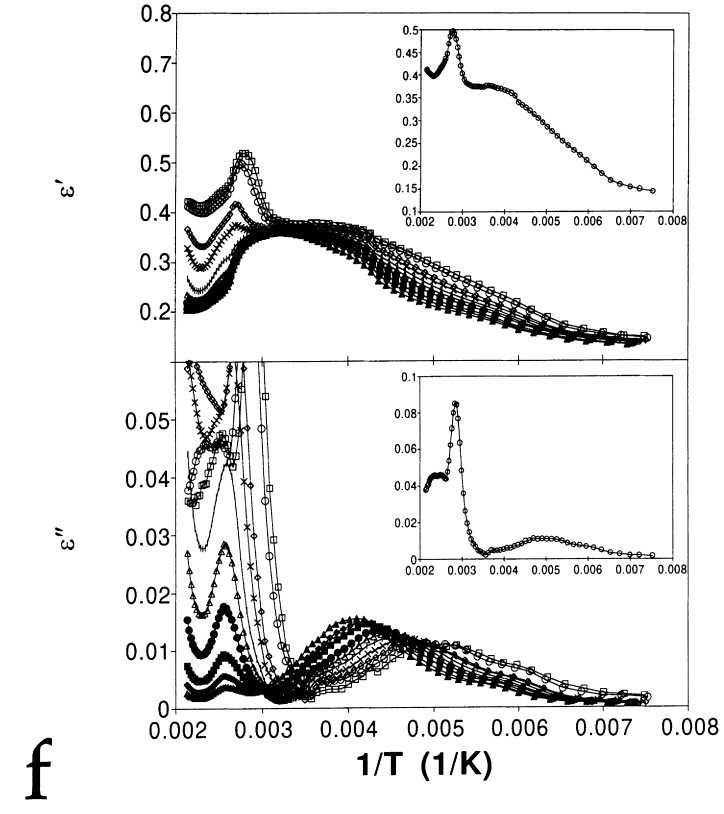

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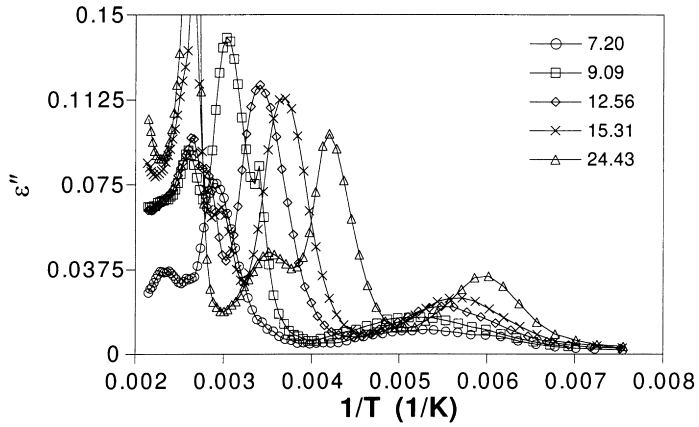


Fig. 3. Dielectric loss spectrum at 100 Hz for granular waxymaize with all water contents studied, showing the major influence of water content on the loss spectrum. The values of water level in the legend are in wt.%.

humidity (the actual water contents are indicated in the figure caption). For ease of comparison, the response at 100 Hz is shown in the inset for each water content. The data are typical of all the starches studied, and no obvious differences were discernible between starches with different biological origins. This result is expected, since the other starches had amylose:amylopectin ratios intermediate between those possessed by amylomaize and waxymaize and the dielectric response of amylomaize and waxymaize are shown to be similar. It is immediately apparent that water content was the prime influence on the dielectric response, demonstrated clearly in Fig. 3, which shows superimposed dielectric loss spectra measured at 100 Hz from granular waxymaize at all water contents studied.

At all water contents at least two relaxations were identified (marked 'β' and 'γ' respectively in Fig. 2), with a third relaxation observed at low frequencies (marked 'α' in Fig. 2) in samples with a high water content (the notation of identifying transitions in order of decreasing temperature is used). At low water contents the γ relaxation became markedly asymmetrical (the asymmetry is most noticeable at higher measurement frequencies, as can be seen in Fig. 2) and appeared to become sub-divided into two separate components (marked 'γ_1' and 'γ_2' in order of decreasing temperature in Fig. 2 for the starch stored in a dry atmosphere). The sharp peak whose position is independent of frequency, and invariably occurred around 100°C, is dielectric loss due to the presence of water. At temperatures above 100°C, the dielectric spectrum became more complex and no distinct relaxations were apparent. Fig. 4 shows the dielectric loss spectrum near the α relaxation for maize starch stored at 97% humidity superimposed on a DSC curve which reveals the operation of the endothermic process of gelatinisation in a similar temperature range. No DSC gelatinisation peak was measured in samples with water contents below approximately 15% (i.e. samples stored in 50% humidity or less).

Fig. 5 shows that the γ_1 relaxation obeyed Arrhenius' law, using granular waxymaize starch as an example. Similar plots for the γ_2 relaxation could not be made since it was not sufficiently well separated from the dominant γ_1 relaxation. The other samples displayed similar behaviour. From

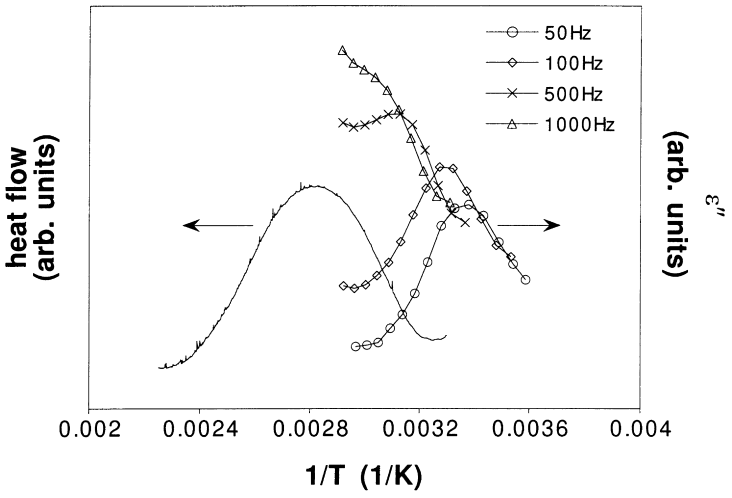


Fig. 4. DSC trace superimposed on the dielectric loss response for granular maize (corn) starch stored at 75% humidity.

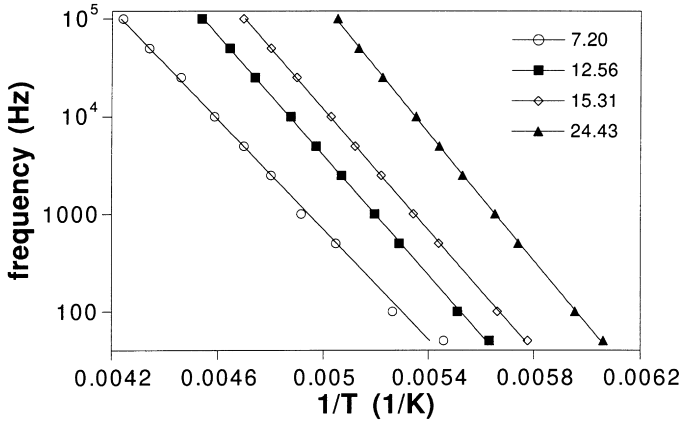


Fig. 5. Arrhenius plots for the γ_1 secondary relaxation in granular waxymaize starch (water contents shown).

the gradient of the graph the activation energy of the relaxation was calculated, and the results for all of the granular starches are displayed in Table 2. Similar plots for the β relaxation were more ambiguous. The overlap with the water loss peak around 100°C made determination of the temperature at which the β relaxation occurred prone to error at measurement frequencies above 1000 Hz. It was therefore impossible to measure a sufficiently large frequency range to establish whether Vogel–Fulcher [13] or Arrhenius behaviour was followed.

3.2. Dielectric response: gelatinised starch

All of the gelatinised starch samples behaved in the same manner as each other, and the relaxations are shown in Fig. 6 for waxymaize starch stored at 0 and 75% humidity and amylomaize stored at 97% humidity (actual water contents are given in the figure caption). The β and γ relaxations that were present in granular starch were observed, as was the splitting of the γ relaxation into two components at low water contents. However, there was neither evidence for the α relaxation that was observed in granular starch, even at the highest water contents, nor a gelatinisation endotherm, measured by DSC. It was noticeable though that the water loss peak was significantly broader (especially at the low temperature side) and stronger than in granular starch.

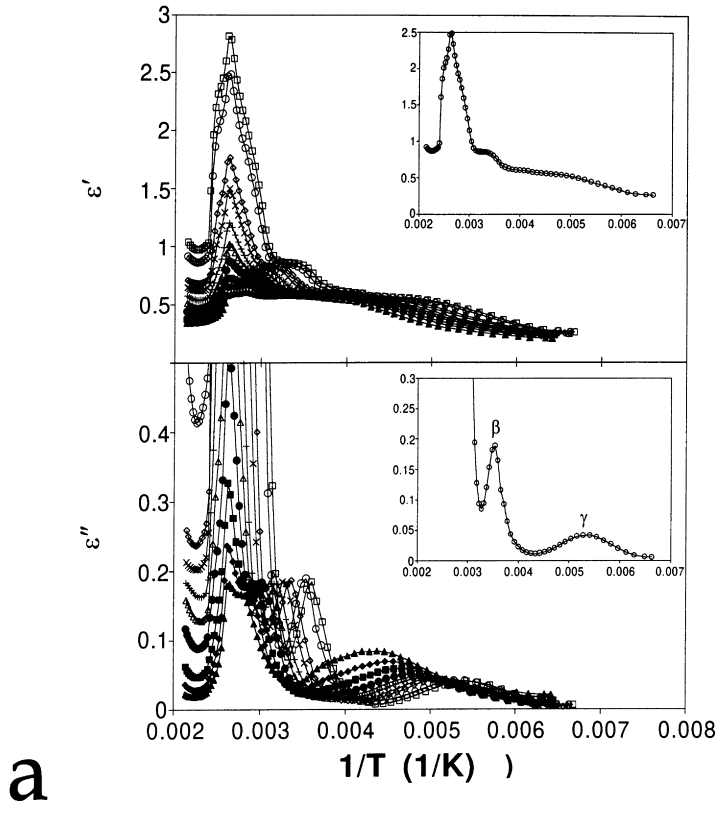
Arrhenius plots were also obtained for the γ_1 relaxation, and the values of activation energy thereby obtained are given in Table 2 alongside the results for granular starch. The problem of the overlap in the loss spectrum with the peak due to water loss with the β relaxation was encountered as described previously, which precluded a more detailed analysis.

3.3. Dielectric response: dextran

Below 0°C the dielectric response of dextran stored at 75% humidity was similar to that of starch; namely a relaxation was observed, the location of which was frequency dependent (see Fig. 7(a)). Above 0°C the behaviour was more complicated. It will not be dealt with here since only

Table 2
Experimentally determined values of the activation energy (in kJ mol^{-1}) of the γ_1 relaxation in starch (±5.0 kJ mol^{-1}). Data for the granular samples are shown above the data for the gelatinised ones. The actual weight percentage water content of the sample is shown in brackets in the cases where sufficient quantities of sample were available for it to be measured by TGA

Sample	% humidity				
	0	11	50	75	97
Amylomaize	62.0 (5.81)	60.4 (9.11)	57.7 (13.03)	58.6 (16.23)	63.4 (24.45)
	58.1 (4.63)			56.8	63.7 (24.72)
Maize (corn)	51.3 (6.33)	55.8 (8.50)	58.3 (11.80)	59.3 (15.25)	57.8 (22.54)
	57.9			58.4 (15.30)	
Potato	56.5 (5.12)	60.4 (9.62)	56.0 (14.69)	59.0 (16.89)	65.5 (27.64)
	(2.02)			(16.04)	
Rice	57.2	56.6 (8.34)	55.4 (12.25)	52.7 (13.70)	54.2
Waxymaize	53.7 (7.20)	50.7 (9.09)	58.6 (12.56)	59.2 (15.31)	62.7 (24.43)
	72.9 (1.86)	62.7 (7.40)	60.0	64.0 (15.68)	
Wheat	58.8 (5.89)	58.5 (8.29)	57.7 (11.83)	56.4 (13.45)	61.8 (24.34)
				52.0 (15.38)	
Dextran				58.9	



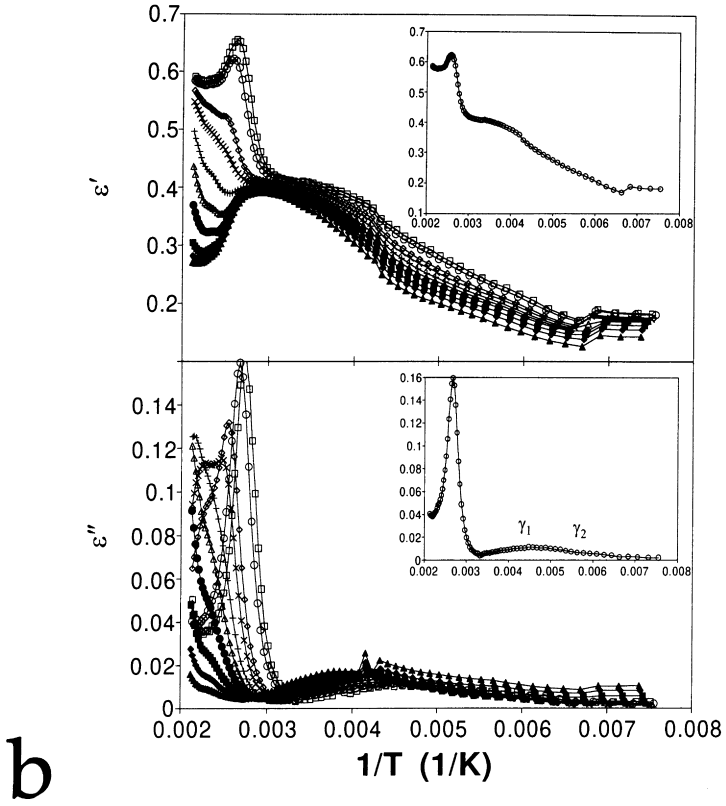


Fig. 6. Dielectric response of gelatinised waxymaize starch stored at (a) 75% humidity (water content 15.68 wt.%), (b) 0% humidity (water content 1.86 wt.%), and (c) gelatinised amylomaize stored at 97% humidity (water content 24.72 wt.%). The inset plots show the dielectric response at 100 Hz. The frequencies in all plots are as marked in Fig. 2(a).

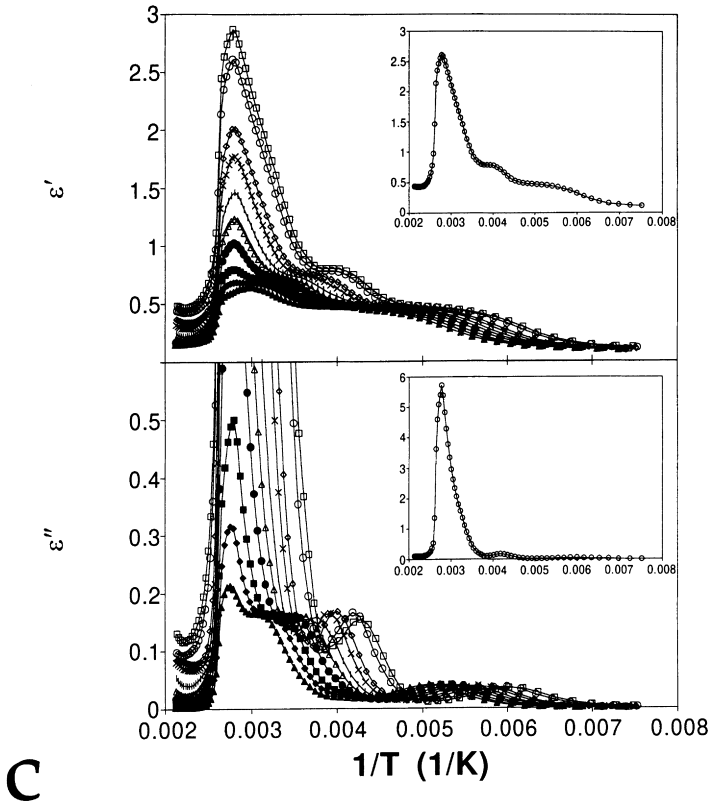


Fig. 6. (*continued*)

the sub-ambient response is relevant to the present study on starch, although it is likely that water loss was responsible for at least part of the dielectric behaviour. Fig. 8 shows an Arrhenius plot for the sub-ambient temperature relaxation (which is to be compared with the starch γ relaxation). 'Dry' dextran exhibited different dielectric behaviour to dextran stored at 75% humidity over the entire temperature range from −140 to 200°C (see Fig. 7(b)). At high temperatures no peak from water loss was observed and at low temperatures there was only a very weak, barely detectable, relaxation (marked '1' in Fig. 7(b) on the plot of ϵ' vs. (1/*T*) and very broad and weak in the ϵ'' vs. (1/*T*) plots). This relaxation was, however, in the general position occupied the γ_1 relaxation in dry starch, and there was no indication in dry dextran of the process denoted γ_2 in dry starch. The relaxation denoted by '2' in Fig. 7(b) on the plot of ϵ' vs. (1/*T*) for dry dextran was associated with the grease in which the dextran powder was mounted; for dry dextran a different type of grease was used which possessed a dielectric relaxation at about −120°C. This relaxation was very sharp and well defined in the ϵ' vs. (1/*T*) plots which distinguishes it from the γ_2 relaxation observed in starch which might be expected to be observed in dextran.

3.4. Positions of the β and γ_1 relaxations in granular and gelatinised starch

The temperatures at which the β and γ_1 relaxations occurred were measured for all samples. Fig. 9 shows the position of the γ_1 relaxation measured at 100, 1000, 10 000 and 100 000 Hz for all starches (granular and gelatinised) as a function of water content. Fig. 10 shows the position of the β relaxation measured at 100 and 1000 Hz (measurement of the position of the β relaxation was unreliable above 1000 Hz since above this frequency it often overlapped with the water loss peak). It can be seen that for a given frequency the results for both relaxations lie on a general curve, found empirically to be best represented by a logarithmic function of water content, regardless of the starch type or crystallinity.

3.5. Debye equation parameters for the γ_1 relaxation in granular and gelatinised starch

Figs. 11–13 display the dependence of the relaxation strength ($\epsilon_R - \epsilon_U$), activation energy (*H*/*R*) and relaxation time τ_0 respectively for the γ_1 relaxation of all of the starches measured at 1000 Hz and obtained by fitting equation (3) (see Appendix) to the experimental data. Similar results for ($\epsilon_R - \epsilon_U$) and (*H*/*R*) were also obtained at the other measurement frequencies (ω), while τ_0 and the quantity $\omega\tau_0$ were frequency dependent (see Table 3 which demonstrates this result using granular waxymaize stored in 75% humidity as an example).

Both the relaxation strength and the activation energy increased in magnitude with increasing water content in a

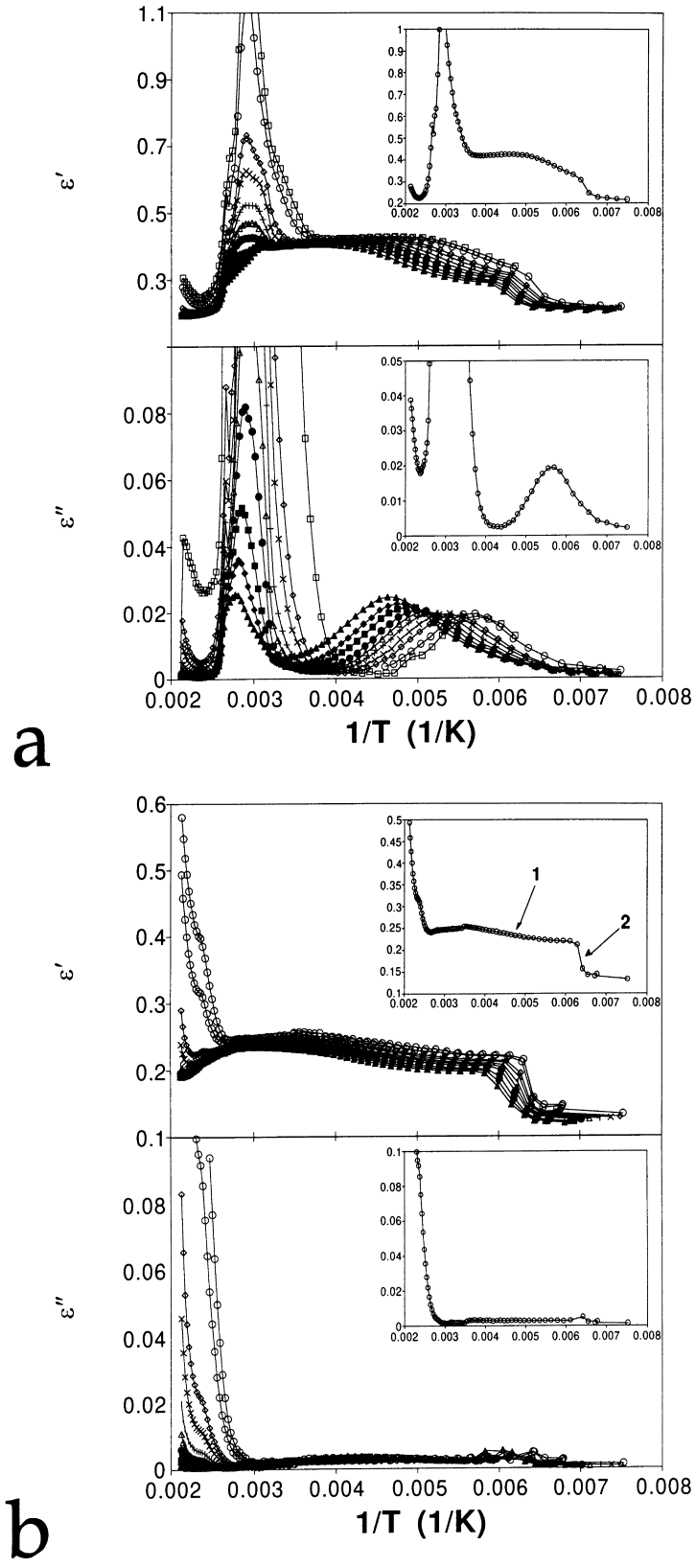


Fig. 7. Dielectric response of dextran stored at (a) 75% humidity and (b) 0% humidity. The inset plots show the dielectric response at 100 Hz. The frequencies in all plots are as marked in Fig. 2(a). Note: The relaxation denoted by '2' in (b) on the plot of ϵ' vs. (1/*T*) for dry dextran was associated with the grease in which the dextran powder was mounted (which was different from that used for 'wet' dextran and all of the starch samples), and should be ignored when considering the response of dry dextran itself (the relaxation denoted by '1' in (b)).

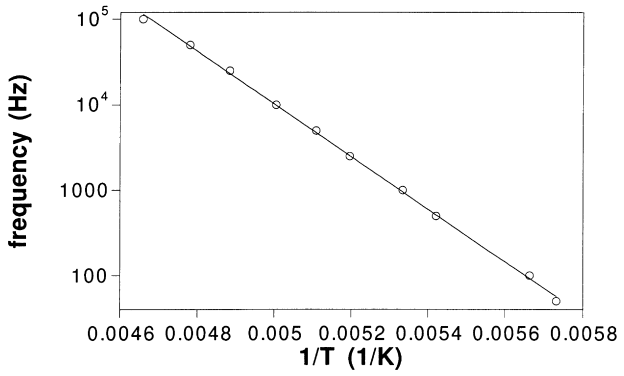


Fig. 8. Arrhenius plot for the secondary relaxation in dextran stored at 75% humidity.

roughly linear relationship. The relaxation time τ_0 decreased with increasing water content, and a linear relationship was obtained between the logarithm of τ_0 and the percentage water content. No major differences in the values of relaxation strength, activation energy or relaxation time at a given water content were apparent between granular and gelatinised starch. It should be noted that, owing to the sample preparation technique leading to the presence of vacuum grease between the plates in the DETA cell, these values are not equal to the 'true' values that would be obtained from a sample of solid starch (which explains the difference in activation energies obtained from the Arrhenius plots given in Table 2—the 'true' values—and those obtained from curve fitting). Nevertheless, the observed trends are considered to remain valid.

4. Discussion

4.1. Overview

From the results presented in this paper it is proposed that the dielectric response of starch may be explained in terms of at least four relaxations. These are the processes referred to, in order of increasing temperature, as relaxations γ_1 and γ_2, β and α respectively, and will be dealt with in that order in the following discussion. In addition, as well as the sharp loss peak at 100°C due to water loss, there were less well defined loss regions above 100°C. There are a variety of explanations for this behaviour; one is that they were due to relaxations specific to the portions of the amylopectin macromolecules comprising the crystalline regions within the granules. However, other reasons, such as conductance loss within these samples at high temperatures, shifting of the glass transition to higher temperatures due to the loss of plasticising water from the sample (in fact in dry amylose literature reports that a glass transition is not measurable since it is so high that the sample decomposes before it is reached [7]), Maxwell–Wagner interfacial polarisation [14] or even factors relating to the particular method of sample preparation, may also have been contributory factors. Owing to the uncertainty, and the inadequacy of the current results to yield definite conclusions, discussion will be limited to the dielectric behaviour measured below 100°C.

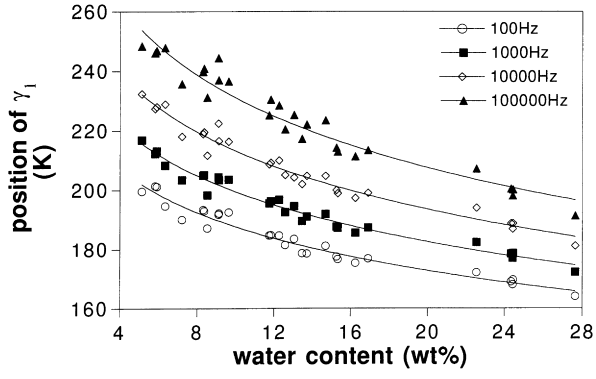


Fig. 9. Dependence of water content on the temperature at which the γ_1 relaxation was observed for all of the different starches (using the four frequencies marked, as examples). The solid lines are best fits of the relaxation temperature as a logarithmic function of water content.

4.2. γ_1 and γ_2 relaxations (secondary relaxations)

A secondary relaxation in amylose has been documented by previous workers, and, as shown in Table 2, the experimentally obtained activation energies (for amylose at least) correspond satisfactorily with the values reported in the literature which range from 40 to 70 kJ mol^{-1} [3–9]. However, from the same literature there is no consensus on the molecular origin for this relaxation. Possible causes of a secondary relaxation in starch are: (i) rotation of hydroxyl groups, (ii) rotation of the methylol group, (iii) localised motions of the chain backbone, including libration of the glucose units about the (1-6)-α linkage and (iv) a boat–chair interconversion of the glucose unit [3–9]. The latter mode has been ruled out on energetic grounds, since a boat–chair interconversion requires both a high activation energy and cooperative motion of several glucose units to occur [5]. The first possibility may also be eliminated, since the experimentally measured activation energy for the secondary relaxation exceeds the value theoretically postulated for hydroxyl rotation (which is about 5 kJ mol^{-1} [4,9]).

Of the two remaining options, mode (iii) may be chosen as the most likely explanation for the dominant γ_1 relaxation on the grounds that the secondary relaxations for both starch and dextran were located at very similar temperatures (taking into account water content) and required very similar activation energies, suggesting that they originate from the same process. Since dextran possesses no methylol groups, option (ii) is eliminated. Therefore the γ_1 relaxation is likely to be due to localised chain motions. Because the strength of this relaxation is directly related to the water content of the sample it may be concluded that it is enabled by the motion of the water molecules which are hydrogen bonded to the amylose and amylopectin molecules. The larger number of water molecules whose motion must be

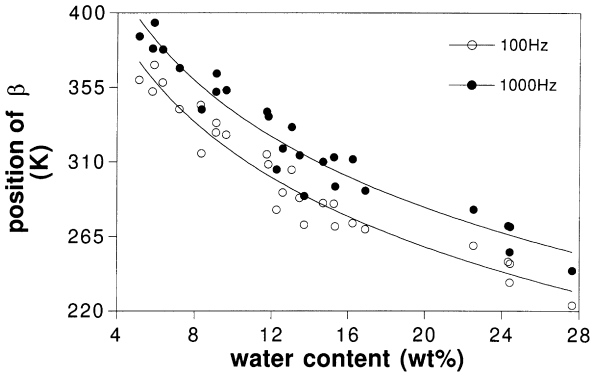


Fig. 10. Dependence of water content on the temperature at which the β relaxation (glass transition) was observed for all of the different starches (using the two frequencies marked, as examples). The solid lines are best fits of the relaxation temperature as a logarithmic function of water content.

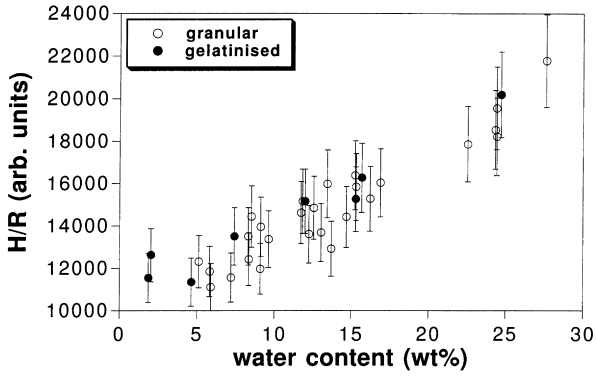


Fig. 12. Fitting results obtained by fitting equation (3) to the dielectric loss spectrum in the region of the γ_1 relaxation: activation energy of the γ_1 relaxation as a function of water content for all starch samples.

enabled also explains the increase in activation energy, as measured from the curve fitting, for the γ_1 relaxation with increasing water content. It should be noted that this trend was not reliably observed from the activation energies measured from the Arrhenius plots. This was probably because of the uncertainty on the figures measured from the Arrhenius plots. More samples must be run to obtain a more accurate average; this was precluded in the present study by the amount of time available. The nature of the small chain motions is uncertain; since the glucose unit is fairly bulky, rotation of the glucose units about the (1-6)-α linkage is unlikely, and rotation about the (1-4)-α linkage is even less likely on account of its lower conformational freedom [7]. Small amplitude oscillations of the glucose rings about the (1-4)-α and (1-6)-α linkages are therefore held to be the most likely cause of the relaxation, although their precise details remain undefined [7].

However, the appearance of another secondary relaxation (γ_2) at low water contents complicates this simple scenario. Two hypotheses qualitatively explain this finding. The first one is that the γ_2 relaxation results from methylol group rotation. If the γ_2 relaxation strength is lower than that of the γ_1 relaxation, and is less influenced by bound water, methylol rotation would only become apparent when the lower water content weakened the strength of the γ_1 relaxation. The γ_2 relaxation would, however, never be observed in isolation; this is partly due to the fact that some small chain motions are always likely to occur and partly due to the impossibility of removing all of the bound water.

In the second hypothesis the operation of methylol rotation is unnecessary. Both γ_1 and γ_2 relaxations are held to result from motions of chains in two different regimes of hydration, a situation known to exist in xylan and chitosan [7,15]. The first, lower temperature, relaxation (corresponding to the γ_2 relaxation in the current scheme) is from 'dry' polymer, and results from the motions of chain segments influenced only by the water that is hydrogen bonded directly to them (at the hydroxyl groups, for instance). As water content increases, the 'dry' polymer process becomes inhibited [16] and eventually overwhelmed by a new one (which would be the observed γ_1 relaxation). The new, 'wet', polymer relaxation is held to result from the motions of chain segments in the presence of water molecules which have associated with others to form a loose hydrogen bonded network, which would explain the heavy dependence of the γ_1 relaxation on water content. The

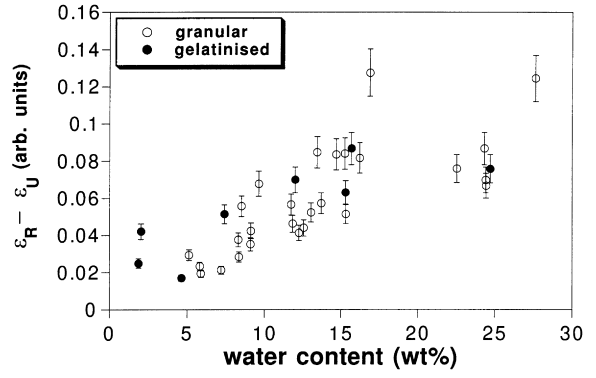


Fig. 11. Fitting results obtained by fitting equation (3) to the dielectric loss spectrum in the region of the γ_1 relaxation: relaxation strength as a function of water content for all starch samples.

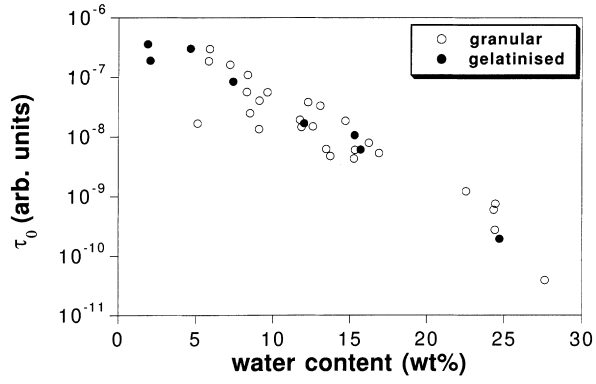


Fig. 13. Fitting results obtained by fitting equation (3) to the dielectric loss spectrum in the region of the γ_1 relaxation: relaxation time parameter of the γ_1 relaxation as a function of water content for all starch samples.

Table 3
Fitting parameters obtained from the γ_1 relaxation for waxymaize stored at 75% humidity: influence of measurement frequency

Frequency (kHz)	$\epsilon_R - \epsilon_U$ (a.u.)	H/R ($\times 10^3$ a.u.)	τ_0 ($\times 10^{-8}$ a.u.)	$\omega\tau_0$ ($\times 10^{-5}$)
0.05	0.047	15.528	6.509	0.325
0.1	0.049	15.216	5.010	0.501
0.5	0.049	15.556	1.207	0.604
1	0.051	15.832	0.608	0.608
2.5	0.053	16.104	0.259	0.648
5	0.053	16.141	0.152	0.760
10	0.054	15.841	0.111	1.11
25	0.055	15.546	0.067	1.675
50	0.054	15.033	0.054	2.70
100	0.055	14.796	0.037	3.70

'wet' polymer relaxation occurs at higher temperatures than the 'dry' polymer relaxation since a greater amount of energy is required to move the chain and the larger amount of associated water. No specific details are given on the actual mechanism of the localised chain motions.

The results from dextran may, however, help in discounting one of these hypotheses. Dextran possesses no methylol groups. Therefore, if the first hypothesis was true, dry dextran would be expected to exhibit only the γ_1 and not the γ_2 relaxation, since the only motions possible would be those of the chain backbone. Since the γ_2 relaxation is indeed absent in 'dry' dextran, the results suggest that the first hypothesis is correct, and that the γ_2 relaxation results from rotation of the methylol group in starch. In fact steric considerations indicate that methylol rotation should be fairly easily performed [3,4,9]. Since the γ_2 relaxation operated at a lower temperature than the γ_1 did, we would conclude that methylol rotation actually occurs more easily than small chain motions. The conclusion of several previous studies has been that it is likely that methylol rotation and small chain motions coexist [3,4,9].

The similar strength of the γ_1 relaxation in gelatinised starch (from which most of the crystallinity has been removed) and the finding that it was not affected by starch type (hence crystalline unit cell or amylose:amylopectin ratio) is contrary to a previous report, in which higher relaxation strengths were found in gelatinised starches and attributed to relaxation occurring in the amorphous regions [5]. It is unclear at present why there is a difference between those results and the data presented in this paper. That the amylose:amylopectin ratio is not important is unsurprising; all of the starches contained amylopectin which possesses both (1-4)-α and (1-6)-α linkages. Therefore chain motions about either of these linkages will occur in amylopectin, and any motion occurring in amylose will be present in amylopectin also. The unimportance of crystallinity is perhaps more surprising. One might expect that relaxations were facilitated more easily in the amorphous regions where molecules have greater free volume and are less constrained by the interchain hydrogen bonds that order the molecules into double helices. However, both granular and gelatinised starches stored in the same humidity atmospheres absorbed similar amounts of water. Since the γ_1 relaxation was governed by the number of water dipoles in the sample, and since these were similar, similar amounts of relaxation were able to occur in granular and gelatinised samples.

4.3. β relaxation

Two explanations exist in the literature for the observed β relaxation. In the first explanation, dehydration of the starch is held responsible for the peak [9]. Its shift to lower temperatures has been explained by the plasticising action of water molecules, although the details of how this relates to dehydration are not clear. However, a stronger relaxation would be expected in the samples containing more water if dehydration was responsible for the β peak; the opposite effect was actually observed.

The second explanation is that the β relaxation is the glass transition and corresponds to an increase in mobility of large portions of the amylose and amylopectin molecules. The glass transition has been studied calorimetrically and mechanically by many authors, and is generally accepted to be located in the region between about 0 and 60°C [1,17] (although the value does depend on water content and measurement technique). The temperature range in which the β relaxation was measured dielectrically was in the same temperature range as this figure, which does not discount the assignment of the dielectric β relaxation to the glass transition. The similar response of both granular and gelatinised starch is surprising upon first consideration, but may simply reflect a similarity in the free volume of the chains in the amorphous regions in granular starch with that possessed by the chains in the gelatinised samples.

As was observed for the γ_1 secondary relaxation, the plasticising effect of water was the main influence on the position of the glass transition temperature, and explains the lowering of the glass transition temperature with increasing water content. This effect has been well documented by other workers [1]. The glucose rings are expected to form networks by hydrogen bonding with water molecules; the decrease in strength of the glass transition with increasing water content (shown in Fig. 3) may reflect the increase in extent of these networks [5].

4.4. α relaxation (gelatinisation)

The term 'gelatinisation' describes the disruption of the semi-crystalline structure of starch in the presence of water. Evidence for gelatinisation being responsible for the α relaxation is provided by the similarity of the temperature range in which it was measured dielectrically with the calorimetrically detected occurrence of gelatinisation in the 'wet' granular starches, and by the absence of the α relaxation in the 'dry' granular and 'wet' gelatinised starches in which gelatinisation is not expected to occur. The apparent measurement of gelatinisation at a higher temperature using DSC may have been due to the higher heating rate of the DSC samples compared with the DETA samples, a difference in water content between the DSC and DETA samples and from the fact that the dielectric α peak was only detectable at lower frequencies (recall that at higher frequencies the water loss signal overwhelmed the α peak). These would have corresponded to the onset of gelatinisation measured by DSC. Therefore, dielectric spectroscopy would appear to reveal the start of gelatinisation, but unfortunately give no indication of the temperature range over which it occurred.

It is known that during gelatinisation amylose molecules leach from the starch granules in which they are contained and that sections of the amylopectin molecules located in the crystalline lamellae dissociate from their bound double helices [1]. Therefore it is likely that the extra mobility that both molecules acquire after release from these constraints is the cause of the α peak in the dielectric loss spectrum. Unfortunately, the limited amount of information revealed by the α peak is not sufficient to distinguish between the different processes that are postulated to occur during gelatinisation, and which are highly dependent upon the water content of the starch (the so-called M1, M2 and G processes [1]).

5. Conclusions

Dielectric spectroscopy has been shown to be a useful tool for probing the molecular relaxation processes in solid starch and dextran (and, by implication, other polysaccharide systems). It has shown the presence of several molecular relaxations in starch which have been identified as follows:

1. At temperatures around 60–80°C in granular starch a relaxation (denoted 'α') occurs which has been roughly correlated with the gelatinisation endotherm from calorimetric measurements, and has been attributed to the increase in mobility of amylose and amylopectin molecules upon swelling of, and release of the molecules from, the starch granules during gelatinisation. This relaxation is absent in pre-gelatinised starch.
2. At temperatures in the region of approximately 0–50°C, a strong relaxation (denoted 'β'), the position of which is highly dependent on the water content of the sample, is present in granular and gelatinised starch. It has been attributed to a major increase in mobility of large segments of the amylose and amylopectin molecules (a glass transition).
3. At temperatures in the region of −120 to −90°C, a relaxation (denoted 'γ_1') obeying Arrhenius' law occurs in granular and gelatinised starch, and dextran. This relaxation is also highly dependent on the water content of the sample, and has been attributed to motions of small parts of the amylose, amylopectin and dextran molecules. The common origin of the relaxation in starch and dextran was inferred from the similar activation energy of this relaxation in all samples, which lay in the region between 50 and 65 kJ mol^{-1}.
4. At temperatures slightly lower than that of the 'γ_1' relaxation, another relaxation (denoted 'γ_2') was observed only in starch with low water contents. From its absence in dry dextran, this relaxation was attributed to rotation of the methylol group present on the amylose and amylopectin molecules in starch.

The major influence on the temperature at which the relaxations occurred, and on the strengths of the relaxations, was the presence of water molecules associated with the amylose and amylopectin within starch. Any influences due to starch type or crystallinity were overshadowed by the influence of water. Water acted as a plasticiser, and it is likely that the relaxations of the amylose and amylopectin molecules were enabled by the motions of the electric dipoles present in the highly polar water molecules bound to amylose and amylopectin. The results highlight the necessity, in hydrophilic material, of investigating samples with a range of known water contents.

Acknowledgements

The assistance of Charles Setterfield, of the University of Cambridge, with the thermal analysis techniques is acknowledged. This work was financially supported by the European Union with funding from the FAIR programme under contract FAIR-CT96-1195.

Appendix A. Dielectric data analysis [10]

If the dielectric relaxation can be described by an Arrhenius' law the dielectric relaxation time, τ_E, at a given temperature, T, may be written as:

$$\tau_E = \tau_0 \exp(H/RT) \quad (1)$$

where H/R is the activation energy of the process. Assuming such Arrhenius behaviour, the Debye equations for a single dielectric relaxation which give the real and imaginary components of the complex permittivity (ϵ' and ϵ''

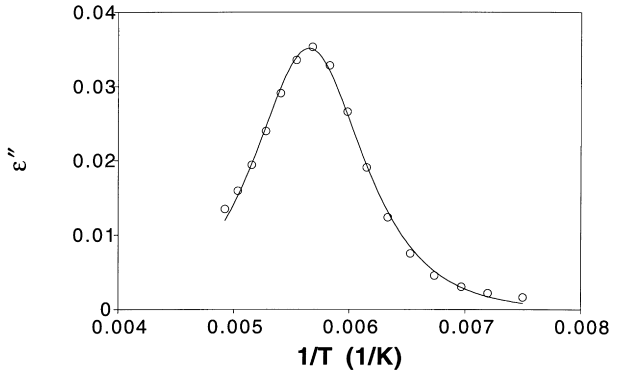


Fig. 14. Example of a fit of equation (3) (solid line) to the experimental dielectric loss data (points) in the region of the γ_1 relaxation: granular waxymaize stored at 97% humidity, dielectric response at 1000 Hz.

respectively) may be written as

$$\epsilon' = \epsilon_U^T + \frac{(\epsilon_R^T - \epsilon_U^T)}{1 + \omega^2\tau_0^2\exp(2H/RT)} \quad (2)$$

$$\epsilon'' = (\epsilon_R^T - \epsilon_U^T)\frac{\omega\tau_0\exp(H/RT)}{1 + \omega^2\tau_0^2\exp(2H/RT)} \quad (3)$$

where ϵ_U^T and ϵ_R^T are the unrelaxed and relaxed permittivities at temperature T respectively and ω is the frequency.

By modelling a dielectric relaxation as a process involving only a single relaxation time, fitting the experimentally determined $\epsilon''(1/T)$ curves by the function given in Eq. (3) allows determination of the relaxation strength ($\epsilon_R - \epsilon_U$), the activation energy (H) and the relaxation time τ_0. This approach was taken for the γ_1 secondary relaxation observed in all the starches and moist dextran (see Section 3), which did obey Arrhenius' law. The experimental data in the region of the γ_1 relaxation was fitted with Eq. (3) using the curve-fitting routines in Kaleidagraph until the best-fit was obtained. Fig. 14 displays an example of experimental data along with the best-fit, as a typical example.

Since Eq. (3) describes a symmetrical function of ($1/T$) and the experimentally determined $\epsilon''(1/T)$ plots for the γ_1 relaxation were also found to be symmetrical, the application of the single relaxation time model to the sub-ambient relaxation may be justified. If there is a distribution of relaxation times, then the values from the fitting Eq. (3) to the ϵ'' data may be regarded as average values from the distribution. Inaccuracies that may arise are likely to occur for the samples with the lowest water contents, owing to the appearance of the γ_2 relaxation. Care was taken in these samples, however, to analyse the portions of the curve where there was minimal overlap of the γ_1 and γ_2 relaxations.

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