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Dielectric studies of amylose, amylopectin and amylose–stearic acid complexes

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ABSTRACT

The effect of structure creation and moisture content on the dielectric properties of amylose, amylopectin and amylose–stearic acid complexes is presented. Three dielectric features have been identified in these systems. At low temperature, a dipole relaxation process is observed which is assigned to the reorientation of the —CH_2OH group. At ambient temperatures, a thermally activated relaxation is assigned to liberation–local chain motion. In certain systems at high temperatures, a Maxwell Wagner Sillars process is observed associated with the heterogeneous nature of media and is ascribed to the gel structure in the amylose–stearic acid complex. The low temperature relaxation is sensitive to the moisture content, the water molecules being bound to the —CH_2OH groups and the activation energy being reduced as the water content is increased. Comparison of the relaxation observed in amylose and amylopectin indicates that chain branching increases the activation energy and inhibits the local reorientation motion of the chain backbone. The relative magnitude of the relaxation processes and their activation energies are discussed in term of the structure of the polymer backbone, the nature of the complex formed with stearic acid and the extent to which order is created by thermal treatment. This paper gives insight into the changes in amylose mobility accompanying the formation of the various complexes.

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1. Introduction

The existence of stable amylose–lipid complexes has been recognised for a number of years (Gidley, 1987; Gidley & Bociek, 1988; Morrison, 1988). Studies of a variety of food processing operations have revealed that the complexes can be formed as a result of many types of preparative operation (De Pilli, Derossi, Talja, Jouppila, & Severini, 2011; Exarhopoulos & Raphaelides, 2012; Tang & Copeland, 2007). Addition of fatty acids alters the physical and chemical properties of starchy foods and is attributed to the formation of the amylose and lipid complexes (De Pilli et al., 2008; Kaur & Singh, 2000; Nebesny, Rosicka, & Tkaczk, 2005; Singh, Cairns, Morris, & Smith, 1998). Stability of the complexes has been identified as an important factor in determining where digestion of the amylose and lipid occurs in the digestive track and this may have health implications (Kawai, Takato, Sasaki, & Kajiwara, 2012; Shelat, Vilaplana, Nicholson, Gidley, & Gilbert, 2011).

Amylose is present in all non-waxy starches and is essentially a linear homopolymer of linked-o-D-glucopyranose residues (De Pilli et al., 2008; Kaur & Singh, 2000; Nebesny et al., 2005; Singh et al., 1998). Three distinct polymorphs of amylose exist and are referred to as the A-, B- and V-forms and the V-form requires the presence of a complexing ligand. The A- and B-forms comprise parallel-packed, left-handed double helices (Imberty, Chanzy, Perez, Buleon, & Tran, 1988). Both these forms contain no internally bound water molecules, but they differ in the packing of the helices into bundles The A-form has a low and the B-form a higher level of water in the interstices. The A- and B-forms can be considered as extended helices with, unlike the V-form, no hydrogen bonding between consecutive turns of the helices. In the V-form, a single chain of amylose forms a helix with a relatively large cavity in which various ligands can be located and the number of glucosyl residues per turn (6, 7 or 8) depends on the ligand. The single V-helical complexes formed from a range of organic ligands and their structures have been reviewed (Gidley, 1987; Gidley & Bociek, 1988). The V-forms have relatively large central cavities with a pitch of about 8 Å per turn, whereas the double helical A- and B-forms have a pitch of about 21 Å and there is no internal cavity. X-ray diffraction (XRD), differential scanning calorimetry and NMR have been used to analyse melting transition characteristics and stability of the complexes (Waigh, Perry, Riekel, Gidley, & Donald, 1998; Jenkins & Donald, 1998; Jenkins et al., 1994; Morrison, Tester, Snape, Law, & Gidley, 1993; Morrison, 1988; Nebesny et al., 2005). The amylose–stearic acid complexes can exist in various forms depending on the conditions and temperature used in their formation (Gidley, 1987; Morrison, 1988; Morrison et al., 1993).

Dielectric characteristics of various forms of starch have reported (Butler & Cameron, 2000) and no significant differences were observed between a number of different types of starch.

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Several dielectric features were observed and attributed to rotation of methylol and short elements of the backbone.

Dielectric relaxation studies are able to reveal the extent to which dipole mobility is changed by the formation of molecular complexes and indicate the temperatures to which these structures must be raised in order that structural changes can occur. For thermally activated processes the temperature dependence of the relaxation frequency is directly related to the activation energy for conformational change. Enzyme attack and related chemical processes can be inhibited by the complex formation. Dielectric measurements will sense the reorientation of polar entities such as the OH and —O— linkages but will also provide information on the mobility of small molecules, such as water dispersed in the matrix. Whereas dynamic mechanical thermal analysis provides on the total chain dynamics and indicates the point at which large-scale motions become active, dielectric relaxation can sense the mobility of the individual dipoles. Dielectric measurements complement NMR studies, however, these latter measurements are difficult to interpret when the groups are hydrogen bonded.

2. Experimental

2.1. Materials

Amylose supplied by Sigma–Aldrich Chemical Company, UK was shown by X-ray analysis to be amorphous. The helix structure was obtained by retrograding amylose and the ^{13}C CP/MAS NMR was used to confirm that the helical structure was formed (Snape, Morrison, Maroto-Valer, Karkalas, & Pethrick, 1998). All the solvents used were analytical grade materials. The amylose as supplied was found to contain 10% H_2O and samples with different moisture content were created by heating a sample at 333 K for 4 h and 433 K for 2 h. A dry sample was also created by storing the material in a vacuum desiccator for 2 weeks over P_2O_5. The samples for measurement were prepared as 1.5 cm diameter disc with thickness typically between 0.05 and 0.1 cm^{-1} using 4000ypsi hydraulic press operated at room temperature.

2.2. Method to produce amylose–lipid complex

The stearic acid–amylose complex (Snape et al., 1998) was prepared using the alkaline route. Stearic acid was used as a model, as its complex with amylose is characteristic of those found with other lipids and it has been extensively investigated previously (Snape et al., 1998). Amylose solution in 0.01 M KOH was prepared using amylose–butanol complex and was mixed with a stearic acid solution in 0.01 M KOH at 358 K to give an amylose–stearic acid ratio by weight of 10/1. The complex was allowed to form at 333 K for 24 h. After three washes with water, the complex was freeze dried and followed by three washes with diethyl ether. The dry complex was re-dispersed in water.

The complex was reformed or recrystallised at 333 K and 363 K separately for 24 h and after dissociation at 423 K for 30 min to obtain form I and form II_l. Form II_l complex was annealed at 388 K for 24 h to obtain form II_h complex. All complexes were freeze dried and washed there times with diethyl ether to remove moisture.

As a reference, a 10% dispersion of stearic acid was prepared in hexatricontane (HC), which was obtained from Sigma–Aldrich UK. The mixture was heated to 353 K and a disc prepared and dielectric measurements performed.

2.3. Dielectric measurements

Measurements were performed using a Solartron 1250 frequency response analyser operating over a frequency range from 0.1 Hz to 6.3×10^5 Hz. A cell which consisted of two pre-etched copper electrodes mounted on an epoxy fibre glass substrate was created. The configuration used generates a three terminal electrode system with an active area of 1 cm^2. The sample discs were clamped between two electrodes and mounted on a heating block in a Oxford Instruments Cryostat (DN 1704). The electrodes were in good thermal contact and isothermal conditions were maintained using an Oxford Instruments ITC4 temperature controller. The method used has been described elsewhere (Hayward, Mahboubian Jones, & Pethrick, 1984). The temperature range studied was 150–440 K and measurements were performed at 10 K intervals. Data was recorded automatically and the frequency dependence of the real $\varepsilon'(\omega)$ and imaginary $\varepsilon''(\omega)$ permittivity calculated at each temperature.

The frequency dependence of the dielectric permittivity and loss was analysed using the Havriliak–Negami equation (Havriliak & Negami, 1967):

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (i\omega\tau)^\alpha)^\beta} \quad (1)$$

where $\varepsilon^*(\omega)$ is the frequency (ω) dependent complex dielectric permittivity, related to the real dielectric permittivity $\varepsilon'(\omega)$ and dielectric loss $\varepsilon''(\omega)$ by $\varepsilon^*(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ and τ is the characteristics relaxation time for the dipole relaxation process, $\Delta\varepsilon$ is the dielectric increment associated with the relaxation, α and β are distribution parameters describing the breadth of the relaxation process. The magnitude of $\Delta\varepsilon$ is related to $\varepsilon_0 - \varepsilon_\infty$ the difference between the low ε_0 and high frequency ε_∞ limiting values associated with the dipolar relaxation process. The experimental data were fitted to Eq. (1), separated into its real and imaginary parts using a MathCAD programme. Variation of τ with temperature allows calculation of the activation energy from Arrhenius plots of the relaxation data.

3. Results and discussion

3.1. Low temperature relaxations

In order to interpret the dielectric studies on the amylose–stearic acid complex, measurements were first performed on amylose, amylopectin and stearic acid. Moisture can interact with the amylose and plays an important part in determining its structure. Samples were prepared with different levels of moisture and the results are presented in Figs. 1–3. The high moisture content sample was obtained by heating the sample at 333 K for 4 h and had a moisture content of 4%. The middle

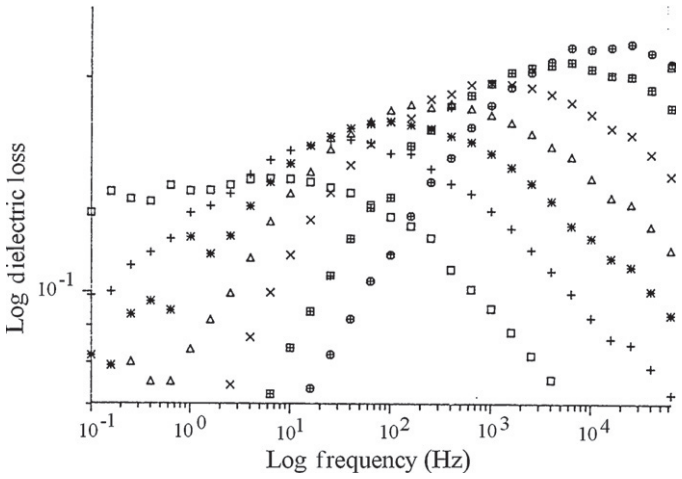

Fig. 1. Dry amylose. *Key*: □, 170 K; +, 180 K; ⊠, 190 K; △, 200 K; ×, 210 K; ⊞, 220 K; ⊕, 230 K.

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