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THE EFFECT OF THE PHASE BEHAVIOUR AND DYNAMICS OF STARCH ON ITS FUNCTIONALITY

Abstract

The phase behaviour and dynamics of starch, and its dextrins, are reviewed. Topics discussed include the effect of diluents on the melting and glass transition behaviour of starch, and factors affecting the dynamics of the starch chain in concentrated systems. The approach adopted is to apply concepts developed in the synthetic polymer area to the biopolymer starch. Finally the relationship between molecular properties and aspects of functionality are examined.

Introduction

Granular starch is usually processed by heating, to achieve disruption of the native, partially crystalline structure. Water and other low molecular weight diluents may be added to facilitate processing or to improve product characteristics. Behaviour is influenced by equilibrium aspects, including how diluents modify the melting and phase behaviour of starch, and non-equilibrium factors, such as the effect of diluents both on the glass transition and plasticization of starch, and on time-dependent changes in properties. The latter may occur, either as a result of crystallization of starch chains, or structural relaxation in amorphous regions. In this review we will not focus entirely on polymeric behaviour as we think that useful insights can be gained by examining behaviour as a function of chain length. We will start by examining phase behaviour.

Phase behaviour

Melting and dissolution

For starch and its dextrins there is a body of experimental data on their crystalline conformations and dissolution behaviour. Even so, the amount of information available

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is not as extensive as for a synthetic polymer. Although the existence of polymorphic crystalline forms of starch has been known for a number of years it is only comparatively recently that it has been possible to obtain single crystals (Imberty and Perez, 1988; Imberty et al., 1988; Buleon *et al.*, 1990; Helbert *et al.*, 1993). The A and B forms, which are present in the native granule, are based on the packing of double helices into monoclinic and hexagonal arrays, respectively.

Although polysaccharides can be crystallized from aqueous solution, it is generally easier to prepare single crystals from oligomeric fragments. The minimum chain length required for the formation of the A and B crystalline forms of starch is greater than 9 units (Pfannemuller, 1987; Gidley *et al.*, 1987). Less information is available on the crystallization behaviour of maltooligomers ranging in degree of polymerisation from 3-9 units. These oligomers readily form stable glasses on drying concentrated aqueous solutions at room temperature (Jeffey and Saenger, 1991; Orford *et al.*, 1989). Methyl α-maltotrioside crystallizes as a tetrahydrate, in which the chain conformation adopted is similar to that found in the A and B forms of amylose (Pangborn *et al.*, 1985). Similarly *p*-nitrophenyl α-maltohexaoside was crystallized as a hydrated molecular complex with $Ba(I_3)_2$, with the carbohydrate chain forming a double helical arrangement (Hinrichs *et al.*, 1987). Recently maltopentaose was crystallized as a hepta or octahydrate (Moates *et al.*, 1997). A characteristic of oligosaccharide hydrates (Jeffey and Saenger, 1991) is that the water forms a network structure, with the sites of occupancy having different affinities for water molecules, and the extent of occupancy depending on ambient conditions of water vapour pressure and temperature.

For synthetic polymers, in extended chain crystals, the melting temperature T_m increases with increasing chain length (Mandelkern *et al.*, 1990). T_m decreases with chain folding, or if the polydispersity of the polymer introduces defects in the crystalline lattice. In contrast to most crystalline synthetic polymers, it is not possible to observe directly the melting of the isolated starch crystals. Even the T_m of the "monomer", anhydrous β-D-glucose, is 150°C (Parks *et al.*, 1928), and close to the temperature at which thermal degradation of carbohydrates is observed. One option for the study of the melting of crystalline forms of starch is to use a diluent to depress T_m (Donovan, 1979). The classical description (Flory, 1953) of the compositional dependence of polymer melting in the presence of a diluent is given by

$$1/T_m = 1/T_m^0 + (R/\Delta H_u).(V_u/V_1).[\,\nu_1 - \chi\nu_1^2] \qquad (1)$$

where T_m^0 is the melting temperature of the pure polymer, V_u and V_1 are the molar volumes of polymer repeating unit and diluent, respectively, ν_1 and ν_2 are the diluent and polymer volume fractions, respectively. ΔH_u is the enthalpy of fusion per repeating unit and χ is the Flory-Huggins interaction parameter characterising the interaction energy per solvent molecule. The above relationship predicts that the smaller the volume of diluent relative to that of the polymer segment, and the more favourable the interaction between diluent and polymer, the greater the effect of the diluent in depressing T_m.

Calorimetric studies (Taylor and Rowlinson, 1955) on carbohydrate/water mixtures show a favourable energetic interaction between the components. With increasing carbohydrate chain length, an opposing entropic contribution to the interaction free energy becomes evident (Moates *et al.*, 1997).

Water at room temperature can be classified as a relatively poor solvent for the starch chain. At the limit of infinite molecular weight, χ is 0.5 for a dilute amylose solution, rising to ~0.8 at a polymer concentration of 80% w/w. These values of χ are qualitatively consistent with the aqueous solution behaviour of the amylosic chain. Although lower maltooligomers form stable aqueous solutions at room temperature, the effect of increasing chain length leads to instability, this is revealed through the gelation and aggregation from concentrated aqueous solution. The solvent quality of water increases with increasing temperature, although as yet there is limited data on the temperature dependence of χ.

The relatively small molecular volume of the water molecule compared to the anhydrohexose unit of the starch chain indicates that it can be an effective diluent in depressing T_m. This is indeed observed in recent studies (Moates *et al.*, 1997) which have examined both the chain length and composition dependence of the dissolution of amylose crystals. The dissolution in water of the B-type crystalline polymorph of amylose, crystallized from fractions of limited polydispersity, ranging in chain length from 12 to 55 residues, was examined by scanning calorimetry. With increasing chain length in this range, the dissolution temperature, at a volume fraction of water of 0.8, increased from 57 to 119°C. The extrapolated dissolution temperature for the high molecular weight polymer at this water content was 147°C. From equation 1 it is possible to obtain a prediction of a T_m of ~250°C at a water content of 26% w/w rising to ~480°C for T_m^0. For the same chain length it was found that the dissolution of the A-polymorph in water occurred at temperatures approximately 20°C higher than the B-polymorph (Whittam *et al.*, 1990). Some of the data on the composition and chain length dependence of melting is summarised schematically in Figure 1. The data is relevant to the stability and processability of starch and its products, and it gives insight into the potential links between starch structure and gelatinization behaviour. It also forms a framework to help interpret the observed retrogradation behaviour of amylose and amylopectin. For example, synthetic polymers in a poor solvent, at a temperature which is far below the T_m of the crystalline solid, often form turbid gels – as does amylose. Similarly, the association between increasing the length of unsubstituted amylopectin constituent chain, and the tendency for amylopectin to recrystallize at ambient temperatures.

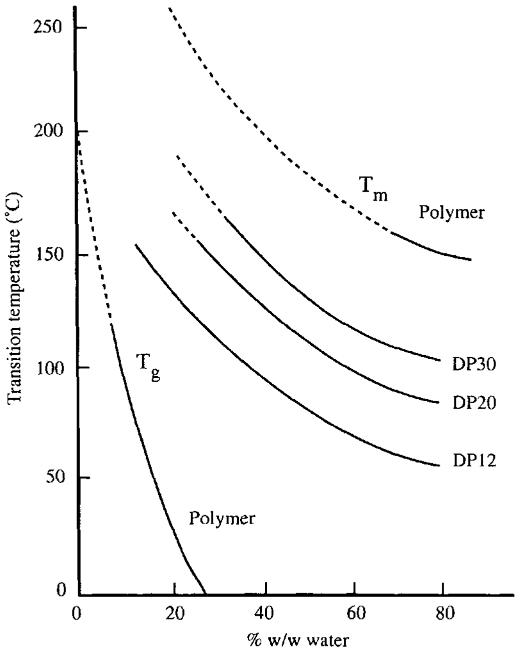

Fig. 1. Composition dependence of the T_m of the B crystalline polymorph of starch in water and T_g of a starch/water mixture. Solid lines denote current limit of observations.

Ternary systems – one polymer and two diluents

Although water is the most common diluent encountered in starch systems, other diluents may be added to further modify behaviour. As water is invariably present, the next step in complexity is to consider behaviour in ternary mixtures, containing two diluents, one of which is water. As before, the balance of interactions between species influences behaviour. When these interactions are sufficiently large, phase separation is obtained, with a polymer-rich phase containing predominantly one diluent, and a polymer-deficient phase containing the other. Even before a phase separation is observed, the partial replacement of one diluent by another can have a dramatic effect on polymer behaviour.

The physicochemical analysis of this phenomenon is dependent on the system, differing somewhat depending on whether a synthetic polymer (Flory, 1953; Altena and Smolders, 1982) or a biopolymer (nucleic acid, protein) is being studied (Arakawa and Timasheff, 1982; Lee *et al.*, 1979; Eisenberg, 1994). An important parameter in both approaches is the pairwise interaction free energy between components. The 'classical approach' as given in equation 1 can be developed to predict phase behaviour in these ternary mixtures (Flory, 1953; Altena and Smolders, 1982). It can also be modified to predict the dissolution of a crystalline polymer in the presence of a diluent and low molecular weight solute (Lelievre, 1976)

$$1/T_m - 1/T_m^0 = R/\Delta H_u \,.\, V_u/V_1\,(v_1 + v_3/x_3 + \chi_{13}v_1v_3 - [\chi_{12}v_1 + (\chi_{23}v_3)/x_3]\,(v_1 + v_3)) \qquad (2)$$

where v_i is the volume fraction of component i and the subscripts 1, 2, 3 refer to diluent, polymer and low molecular weight solute respectively, with the quantity x_3 the ratio of the molar volume of this solute to the molar volume of diluent. The effect of diluents on depression of T_m is therefore dependent on the various interaction parameters, χ_{12}, χ_{13}, χ_{23}, and the relative sizes of the diluents. As before, the interaction between diluent and polymer is characterized as the interaction per polymer segment. In the dissolution of crystalline forms of starch, at a fixed volume fraction of polymer, the replacement of water by D-glucose or sorbitol is predicted to lead to an increase in T_m, simply as a result of the replacement of a relatively small diluent (water) by a larger one which can only interact weakly with the starch chain. Conversely, to observe a depression in T_m, a relatively strong attractive interaction, χ_{23}, is needed to counteract the replacement of water by a larger solute. An illustration of these effects is given in Figure 2 which shows the effect of added diluents on the T_m of a crystalline amylose fraction. For diluents which interact weakly with the starch chain (glycerol, D-glucose, sorbitol) the addition of a larger diluent elevates T_m. For diluents which have a stronger attractive interaction (urea, guanidinium thiocyanate) a depression in T_m is observed. The validity of the approach requires more research.

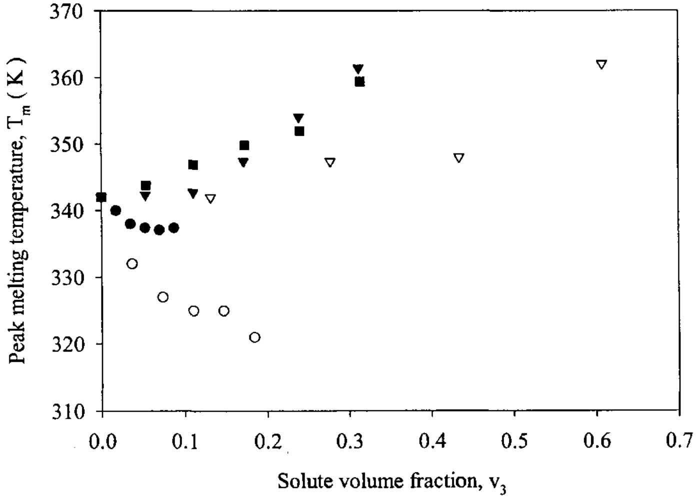

Fig. 2. T_m versus solute volume fraction for the dissolution of amylose crystallites in a ternary aqueous mixture for the solutes, glycerol (▽); sorbitol (■); D-glucose (▽); urea (●); guanidinium thiocyanate (○).

Dynamics

Glass transition behaviour of starch

A glass has a liquid-like structure without obvious mobility. As a material is undercooled below T_m, and providing crystallization does not intervene, its viscosity will progressively increase. If the viscosity is so large, that the material cannot flow within a practical timescale, it will have solid-like characteristics. Typically this occurs at viscosities in excess of 10^{12} Pas when the shear stress relaxation time is of the order of 100s. The transition from solid-like to liquid-like behaviour occurs at the glass transition temperature, T_g. As the heat capacities of glasses and supercooled liquids differ, calorimetry is a convenient method for the measurement of T_g from the 'step' change in heat capacity. The solid-like to liquid-like transition will occur at different temperatures depending on the timescale imposed by the experimental procedure. The glass transition behaviour of D-glucose was examined over 60 years ago when a T_g of 7°C was found (Parks *et al.*, 1928, 1934). More recently, the glass transition behaviour of a maltooligomer series was examined (Orford *et al.*, 1989). T_g increased with increasing degree of polymerization and reached 173°C for maltohexaose. Again this is close to the temperature at which thermal degradation of carbohydrates becomes apparent, with a result that the T_g of amorphous starch cannot be determined directly. A plasticizer has to be used to depress T_g and the glass transition behaviour examined as a function of composition. In starchy materials, water has a very marked effect on depressing T_g. For example, the addition of just 6% w/w water to dry maltohexaose (about 0.8 water molecules per anhydrohexose unit) depresses T_g by about 100°. The composition dependence of T_g for a high molecular weight starch polysaccharide is summarised schematically in Figure 1. The T_g of starch/dextrin water mixtures shows, compared to T_m, a weak dependence on chain length.

There is more limited information on the effect of other plasticizers on the T_g of starch. One of the more widely studied is glycerol. A 88% starch/water mixture had a T_g of ~ 70°C. To achieve the same depression in T_g it was necessary to add > 29% w/w glycerol to starch, glycerol can therefore be considered to be a less effective plasticizer than water. As water was added to these mixtures, the behaviour became more complex, with the appearance of two separate glass transitions. The major component involved in one was thought to be starch, for the other glycerol. The most likely explanation was that there had been some sort of phase separation with the formation of starch-rich and glycerol-rich phases (Forssell *et al.*, 1997). Further research is necessary to confirm this suggestion.

Structural relaxation and localised motions

The relationship between viscosity and molecular mobility is relevant to practical usage of starch in several ways, including mechanical properties; the stability of the material to crystallization; the encapsulation performance of starch and maltodextrin matrices; and the ageing of amorphous materials. As a background to these phenomena, it is useful to examine the dependence of viscosity, η, on temperature, T, as the liquid is undercooled. For simplicity we only describe the behaviour of a low molecular weight non-entangling system which exhibit Newtonian viscous behaviour. Higher molecular weight materials have more complex non-Newtonian rheologies, however broadly similar concepts still apply. The behaviour of many organic liquids, (including the carbohydrates - D-glucose (Parks *et al.*, 1934), glucitol and maltose (Angell *et al.*, 1982; Noel *et al.*, 1991)) can be described by an empirical expression of the type

$$\eta = \eta_\infty \exp (B/(T-T_0)) \qquad (3)$$

where η_∞, B and T_0 are constants. As T_g is approached there is a very strong dependence of viscosity on temperature.

The enormous viscosity of glassy carbohydrates has led to their use as matrices for the encapsulation of active agents, including flavours and pharmaceutical products. While the glass is often mechanically stable for months, deterioration can occur through moisture sorption and plasticization of the matrix, which can accelerate the rate of crystallization. Crystallization of the carbohydrate can concentrate the active agent leading to loss. A topic of current interest is the extent to which mobility persists in the glass, and the supercooled region above T_g, and the effect of this mobility on chemical and enzymic reaction. To start to tackle this topic it is necessary to examine in more detail the dynamics of these undercooled liquids.

The reorientational dynamics of the carbohydrate in the undercooled liquid can be probed by NMR (Girlich and Ludemann, 1993) and dielectric techniques (Noel *et al.*, 1996a). For pure maltose two main dielectric relaxations are observed. The primary relaxation, at the higher temperature, is ascribed to reorientation of the whole molecule, at a rate influenced by the bulk shear viscosity. This relaxation is therefore a direct probe of viscosity, and is intimately linked with the glass transition. The secondary relaxation, at the lower temperature, is ascribed to a more localised motion. NMR and further dielectric experiments on other carbohydrates suggest that this localised motion is linked with the reorientation of the pendant hydroxymethyl group at C-6. Addition of water, with its plasticizing action, to the maltose, shifts the primary and secondary relaxations to lower temperatures, with a marked increase in the strength of the secondary relaxation. This suggests that water is relatively free to reorient within the maltose matrix and is consistent with the observed diffusive behaviour of water in these systems.

In addition to identification of the link between molecular structure and dynamics there is also important to consider in more detail the structure of the amorphous liquid and its dependence on temperature. Such information can be obtained by wide-angle neutron scattering combined with H/D isotopic substitution. In a recent study (Tromp *et al.*, 1997) on amorphous D-glucose, it was found that the number of hydrogen bonds in the glass were more or less similar to that in the crystal. On heating the undercooled liquid, there was a fall in number of hydrogen bonds coupled with a restructuring of the hydrogen bond network. Presumably one potential effect of any added plasticizer is disruption of this network.

For species which are large relative to the molecular length scale, an increase in viscosity will lead to a comparable reduction in diffusion. As size is reduced and approaches molecular dimensions, an uncoupling of diffusion from viscosity can be observed. As yet there are few measurements on carbohydrate liquids. One example is shown schematically in Figure 4 where the mutual diffusion in maltose/water mixtures is compared to the viscosity increase on undercooling. As T_g is approached, a dramatic uncoupling of diffusive and viscous behaviour is observed, with diffusion in the undercooled liquid being much more rapid than expected (Parker and Ring, 1995). Other ways of probing transport processes, such as the measurement of ionic conductivity, yield comparable data (Noel *et al.*, 1996b). There is a need for further measurements which determine the effect of molecular size on the observed uncoupling.

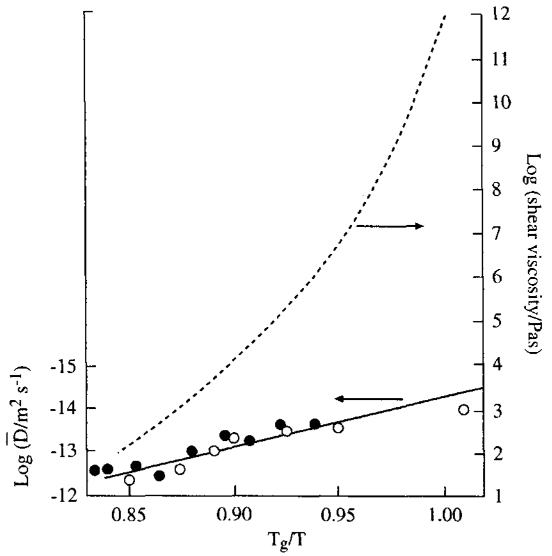

Fig. 4. Comparison of viscous and diffusive behaviour in maltose/water mixtures as the glass transition is approached.

Although this discussion has concentrated on low molecular weight carbohydrates, for which data is emerging, it is to be expected that studies will be extended to polysaccharides such as starch.

Functionality of starch

As a texture modifier

Starch often makes a major contribution to food texture. Several types of microstructure can be produced. For example after heating a moderately concentrated starch suspension (~ 6% w/w) above its gelatinization temperature a starch paste is formed consisting of swollen gelatinized starch granules dispersed in a liquid containing solubilised starch polysaccharides, chiefly amylose (Evans and Haisman, 1979; Doublier *et al.*, 1987; Ellis *et al.*, 1989; Svegmark and Hermansson 1991). The rheological properties of this material is influenced by the volume that the granules occupy and their deformability and shape. The contribution of the solubilised material to the rheological properties is, at this stage, rather small.

If the paste is cooled the solubilised amylose can, if sufficiently concentrated, aggregate to form a gel network (Miles *et al.*, 1985a; Gidley, 1989; Gidley and Bulpin, 1989). As the stiffness of this network is very dependent on amylose concentration, the amylose can make a major contribution to the elastic properties of the starch gel. The swollen granules reinforce this gel by acting as a filler (Miles *et al.*, 1985b). The crystallization of amylopectin on aging (Ring *et al.*, 1987; Shi and Seib, 1992; Wursch and Gumy, 1994) increases the stiffness of the granules and the overall stiffness of the starch gel.

As a nutrient

As well as making an important contribution to food texture starch is a major dietary polysaccharide. There is a need to understand the factors affecting digestibility in the gastrointestinal tract. Although there is a substantial literature on the physical chemistry of how enzymes attack polymers in solution, other factors influence the attack of solid and semi-solid materials. For dense solids, attack can only occur at the solid liquid interface. An important factor relevant to the rate of enzymolysis is therefore the amount of interface rather than the concentration of substrate. For the enzyme to attack the solid it needs to bind to the surface (Leloup *et al.*, 1991,1992a). Access to the surface substrate may be somewhat restricted reducing the affinity of the enzyme for its substrate. This has two effects. Firstly, to achieve surface saturation, and therefore maximal rate of attack, relatively high concentrations of enzyme in solution may be required. Secondly, in mixed systems, with some of the substrate in soluble form and some as a solid, the higher affinity of the enzyme for the soluble substrate will lead to its preferential attack. An additional factor is the difference between starch conformation in the solid and solution. Starch in solution has a flexible conformation which can fit into the active site of the enzyme. In the solid state, flexibility is reduced and other conformations e.g. double helical, may be present which reduce enzyme substrate binding and catalysis. For processed starch which has been allowed to partially crystallize, the amylose double helix is resistant to amylolysis (Colquhoun *et al.*, 1992). This resistant fraction can modify the digestibility of the starch substrate. For network solids which are to some extent porous to the enzyme, additional factors affecting the rate of enzymolysis include the fraction of the network which is accessible to molecules the size of the enzyme, and the effect of the network on the diffusion of the enzyme (Leloup *et al.*, 1990, 1992b).

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WPŁYW ZACHOWANIA FAZOWEGO I DYNAMICZNEGO SKROBI NA JEJ FUNKCJONALNOŚĆ

Streszczenie

Dokonano przeglądu fazowego i dynamicznego zachowania się skrobi i dekstryn z nich. Omawia się wpływ rozcieńczania na topnienie i zeszklenie skrobi oraz czynniki wpływające na dynamikę łańcuchów skrobiowych w układach stężonych. Przyjęto podejście stosowane do polimerów syntetycznych. Sprawdzono zależność pomiędzy właściwościami molekularnymi i pewnymi cechami funkcjonalności.