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A review of thermal analysis studies of starch gelatinization

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Abstract

The gelatinization of starch is an important operation in the food industry. The present review shows that thermal analysis studies have proved to be a powerful means of probing the process. Thermal analysis demonstrates that glass and melting transitions take place when aqueous starch systems are heated and that water influences the temperature of these events.

Keywords: Calorimetry; DSC; Gel; Gelatinization; Glass transition; Melting; Starch; TMA; Water

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1. Introduction

Starch polysaccharides have been investigated for many years. Indeed these molecules were among the first polymers to be studied. Early work demonstrated the presence of two kinds of polysaccharides in starch, namely amylose, which is essentially linear, and amylopectin, which is highly branched. Both macromolecules are composed of glucose units and occur in plant tissues in the form of granules. The granules contain crystalline and amorphous domains. The finding that the polysaccharies form double helices, which underlie the crystalline structures, is considered to be one of the pivotal events in the history of starch chemistry [1].

Starch provides a high proportion of the world's food energy intake. Before consumption, starchy food materials are generally heated to a stage where a transition

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known as gelatinization occurs. Thus gelatinization is an important operation in food preparation and processing. The transition entails a loss of structural order. The starch double helices disappear [2] though some of the resultant polysaccharide coils may form a different helical structure by interacting with lipids [3].

A long established trend in food research is to take the principles underlying and the methods of studying synthetic polymers, and to apply these to food systems. Thermal analysis techniques provide powerful methods of probing the transitions that take place when synthetic polymers are heated [4]. Thus it is not surprising that such methods have been widely used to study gelatinization. Differential scanning calorimetry (DSC), isothermal calorimetry and thermomechanical analysis (TMA) have been employed. The data thus obtained have been interpreted in terms of theories of glass and order–disorder transitions.

At present, the interpretation of thermal analysis measurements of gelatinization is a question of debate [5,6]. This review is restricted to a discussion of the nature of both the glass and melt transitions taking place when aqueous starch suspensions are heated. Detailed discussions of other aspects of gelatinization are available elsewhere [7,8].

2. DSC measurements

2.1. Endothermic transitions

The most prominent feature of DSC traces is an endothermic peak or peaks in the temperature range associated with gelatinization. At relatively high water levels, where the volume fraction of polysaccharide is less than about 0.5, a single endotherm is apparent which is centred at about 330 K [9]. The precise position of the peak depends on the variety of starch being investigated [8]. As the volume fraction of polymer is increased, two endothermic peaks become apparent. The first is at the same temperature as in the more dilute case. The temperature of the second increases as the water content decreases [9]. If the volume fraction of polymer is raised still further, the lower temperature endotherm largely disappears while the temperature of the second continues to rise [9]. In addition to the aforementioned peaks, transitions due to lipid–amylose complexes are found at about 393 K. Again the exact position of the peak depends on the moisture content. The formation of lipid–amylose complexes has been discussed extensively by Biliaderis [8] and will not be considered further here.

Endotherm shape is also a function of the heating rate. In the case of dilute systems, as the heating is increased the single peak moves to a higher temperature and broadens [10]. The starting point of the endotherm is practically independent of the heating rate [10]. With more concentrated suspensions a different set of changes is evident [11]. As the heating rate is increased, the endothermic transition shifts to a higher temperature and fewer peaks are apparent.

The remaining factor known to influence endotherm shape is the sample size. The larger the sample size, the more likely a single peak is to be evident, suggesting that changes in instrument resolution may be occurring [11].

2.2. *Baseline shifts*

Baseline shifts, indicative of heat capacity changes, have been detected in DSC traces. The first takes place at temperatures well below the gelatinization point [12]. As water is added to a dry sample, the temperature of the heat capacity change decreases rapidly, and once the water level is greater than about 20% the baseline shift occurs below room temperature [13]. Comparison of granular and pregelatinized starches demonstrates that in the partly crystalline sample the temperature of the baseline shift is higher [12]. This would be expected from synthetic polymer experiments. The heat capacity change is reversible in that the starch polymer may be heated above and then cooled below the point of the baseline shift, and on reheating the shift occurs again [12].

Another baseline shift takes place in the region of the gelatinization endotherm. However the precise position of this shift is a question of debate [5]. The first reports suggested that the event is located at the start of the gelatinization peak because qualitative X-ray measurements appeared to show that melting does not take place at this stage [14]. However quantitative X-ray crystallinity data indicate that a major DSC transition does not take place in the absence of a melt [15]. A recent study by Cooke and Gidley confirms that the enthalpy change at the start of the endotherm is accompanied by a crystallinity decrease [2]. Another report suggested that the heat capacity change is located exclusively at the leading edge of the first DSC peak because, after heating to any given temperature in this region, rescanning gives a baseline shift between the first and second scans [13]. Furthermore rescanning after heating to the peak maximum yields a comparatively symmetrical endotherm with a relatively flat baseline [13]. This was considered to represent the melting transition of microcrystalline regions of fully water-plasticized starch. However, the data in the report [13] show that when the initial scanning temperature is increased further the baseline difference at the start of the two scans continues to increase [16].

The heat capacity/endotherm relationship can also be studied [16] by a modification of the method of Slade and Levine [13]. The procedure entails heating the sample to a given temperature, cooling to the starting point and rescanning to about 420 K. The difference between the two scans is then computed. The maximum temperature reached in the partial initial scan is first kept below that at which the endotherm begins. In subsequent runs this maximum is gradually raised until the end point of the DSC trace is reached. The procedure clearly demonstrates that the heat capacity change starts at the same point as the endotherm and increases in size until the phase transition is complete [16].

3. Isothermal calorimetry measurements

A very small difference between the heat capacity of gelatinized and native starch has been found by isothermal calorimetry [17]. A high degree of uncertainty was associated with the results.

4. TMA measurements

Measurements have been made of the thermal expansion of aqueous dispersions of granules over the range in which gelatinization occurs. Biliaderis et al. demonstrated that in concentrated mixtures a two-stage process is present [18]. The temperature range of the initial stage of expansion roughly corresponds to the leading edge of the endotherm while the final, more rapid, stage appears to take place towards the completion of the melting, as signalled by the levelling of the DSC trace. An exact comparison of the DSC and TMA data obtained in this study is not possible because the heating rates used to obtain the data were not the same. Recent work suggests that the changes detected by TMA parallel decreases in crystalline order [15]. There appears to be no published work on the thermal expansion of relatively dilute suspensions, presumably because of experimental difficulties.

5. The glass transition in starch

All researchers appear to agree that a glass transition takes place in starch–water systems. With pure starch the precise temperature is uncertain because thermal degradation of the dry polymer precludes measurement of T_g [6]. Extrapolation from the T_g values for dry malto-oligosaccharides suggests that the high molecular weight limit is of the order of 500 K [19]. Extrapolation from measurements on starch–water systems also indicates that the T_g for pure starch is about 500 K [20]. The T_g decreases by about 6 K per % water for the first 10% water addition [21], which is in agreement with the free volume theory [22]. Once the water content reaches about 20% the starch is plasticized at room temperature. As the water content increases further, T_g continues to decline and is eventually below the freezing point of the aqueous system.

There is some debate about the meaning of the heat capacity change accompanying gelatinization [5]. The recent DSC study of Noel and Ring demonstrated that the amorphous regions of granules are fully plasticized at the onset of gelatinization [6]. Thus a glass transition is not taking place in this region. This would be expected because the glass transition occurs below ambient temperature once the moisture content exceeds about 20% [21]. In most synthetic polymers the glass transition takes place at a much lower temperature than the melt transition [4].

A central feature of the original model, proposing that the heat capacity change accompanying gelatinization is associated with a glass transition, was that an imbalance of water inside (10% (w/w)) and outside (100% (w/w)) the granule was considered to occur [13]. However there is extensive evidence demonstrating that sufficient water is present to plasticize the starch particles at ambient temperatures [5]. Advocates of the super-heated glass explanation of gelatinization therefore suggested that the water in the granules is present without causing plasticization [22]. Nevertheless, the fact that granules can be annealed below the gelatinization temperature demonstrates that they must be plasticized [16]. The fact that annealed samples show a DSC baseline shift when they melt, as do fully plasticized starch gels, further adds to the evidence that the heat capacity change accompanying gelatinization is not due to a glass transition [16]. The molecular events responsible for this heat capacity difference have yet to be established. One suggestion is that the change is attributable to the displacement of hydrogen bonds between starch crystallites and water molecules [17].

6. The melting transition in starch

It has long been recognized that under real-world heating conditions, gelatinization is a non-equilibrium transition [9,13,24–26]. The non-equilibrium conditions occur for several reasons [5]. Firstly, the polymer and diluent are not intimately mixed and water gradients occur in the sample [25]. Secondly, DSC heating rates are too fast to prevent superheating of the sample [9]. Thirdly, there is insufficient time for annealing to produce the requisite equilibrium crystals [26]. Indeed the branching in amylopectin may inhibit crystal growth to the point where surface free energy effects are always present. Thus equilibrium theories of starch gelatinization are based on a highly idealized model of the transition and can predict trends in, but not the thermodynamic parameters associated with, the process.

A large number of explanations of the molecular processes responsible for gelatinization has been proposed [5,8]. These have served to challenge the ideas about starch behaviour prevalent at the time in question. However as the knowledge base has developed, many of these explanations have been superseded.

In a recent study by Cooke and Gidley, the origin of the starch gelatinization enthalpic transition was investigated [2]. Samples were studied by DSC, NMR and X-ray diffraction. The work suggests that crystalline and helical order are lost concurrently during gelatinization. Thus models which invoke crystallite disruption followed at a higher temperature by helix melting [27], are not consistent with their observations. In addition, no evidence was found for the melting of non-crystalline helices at a temperature lower than that of crystallite melting. Thus suggestions [28] that the thermal stability of starch helices is affected significantly by the presence or absence of a crystalline environment are not consistent with the experimental findings. The other major finding of Cook and Gidley [2] was that the enthalpy of gelatinization primarily reflects the loss of molecular (double-helical) order.

The melting explanation of gelatinization suggests that crystalline (or helical) zones in different granules have different stabilities [16,25]. It is suggested that water migrates from one location to another as the various granules gelatinize. Thus the DSC peaks correspond to melting transitions of crystalline material with different stabilities, at different diluent levels. According to the model, if the water content of the suspension is sufficiently high, i.e. above about 65%, each granule will absorb water without restriction and a single endothermic peak is observed. If the water content is less than this level, there is competition by the granules for water. In this case the least stable granules melt first, absorb water and so deplete the remainder of the diluent. The latter particles melt at higher temperatures partly because they are more stable and partly because the effective volume fraction of diluent is reduced. The endotherm associated with the higher melting point fraction initially occurs in the form of a trailing shoulder on the first peak. As the water content of the sample is reduced further, fewer granules are able to gelatinize in an unrestricted water environment and so the first endotherm decreases in size while the second increases and shifts to a higher temperature. If the volume fraction of water is reduced sufficiently, only the higher temperature endotherm is apparent.

Support for the concept that water migration influences the shape of endotherms comes from experiments in which blends of starches with known differences in gelatinization temperature ranges have been studied [29]. By altering the ratio of the two starches in the blend the competition for water can be altered in a way predicted by the melting explanation of gelatinization. With high heating rates, there is insufficient time for water redistribution and the DSC traces change accordingly [11]. X-ray studies [15] do not support the view [18] that DSC traces change with heating rate as a result of polymer recrystallization.

7. Conclusions

Thermal analysis methods, supported by other techniques, demonstrate that starch systems show two characteristic transitions on heating. The first is a glass transition in which kinetic factors play a role. As the temperature is raised considerably further, an order–disorder melt transition takes place. Water has a marked influence on the temperature of both.

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