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Effect of high molecular weight plasticizers on the gelatinization of starch under static and shear conditions

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ABSTRACT

Starch gelatinization in the presence of high molecular weight polyol plasticizers and water was studied under static and dynamic conditions and was compared to a glycerol reference. For static gelatinization, glycerol, sorbitol, diglycerol and polyglycerol were examined using polarized light microscopy and differential scanning calorimetry. A wide range of starch/water/plasticizer compositions were prepared to explore the gelatinization regime for each plasticizer. The plasticizers show that the onset and conclusion temperatures for sorbitol and glycerol are in the same range and are lower than the other two plasticizers. On the other hand, polyglycerol shows a higher gelatinization temperature than diglycerol because of its higher molecular weight and viscosity. The results indicate that in the case of all plasticizers, increasing the water content tends to decrease the gelatinization temperature and, except for polyglycerol, increasing the plasticizer content increases the gelatinization temperature. In the case of polyglycerol, however, increasing the plasticizer content had the opposite effect and this was found to be related to the borderline solubility of polyglycerol in water. When the polyglycerol/water solubility was increased by increasing the temperature of the water/plasticizer/starch slurry, the gelatinization temperature dependence was found to be similar to the other polyols.

A rheological technique was developed to study the dynamic gelatinization process by tracking the influence of shear on the complex viscosity in a couette flow system. Glycerol, diglycerol and sorbitol were subjected to different dynamic gelatinization treatments and the results were compared with static gelatinization. It is quantitatively shown that shear has a major effect on the gelatinization process. The conclusion temperature of gelatinization is significantly diminished (up to 21 °C) in the presence of shear whereas the onset temperature of gelatinization remains virtually unchanged as compared to static conditions. By comparing glycerol, diglycerol and sorbitol data, it is shown that the molecular weight or structure did not qualitatively affect the changes shear imposed on dynamic gelatinization. Shear had a relatively more pronounced effect on diglycerol as the plasticizer with less hydrogen bonding ability.

1. Introduction

Starch is a natural homopolymer of two different structural units of α-D-glucose: amylose and amylopectine. These two subcategories are responsible for the crystalline structure of starch which, along with their high molecular weight ($\sim 10^6$–10^7 Da) (Angles & Dufresne, 2000), cause starch to decompose before reaching its melting point. Due to this characteristic, starch has been used as a filler in the polymer industry for many years (Avella et al., 2000; Averous, Moro, Dole, & Fringant, 2000; Averous, 2004; Lawrence, Walia, Felker, & Willett, 2004).

The crystalline starch structure is lost when it is subjected to heat at temperatures greater than 70–90 °C in presence of plasticizers such as water or glycerol. This process is called gelatinization (Otey, Westhoff, & Doane, 1980). Gelatinization is associated with the loss of double helices together with the loss of lamellar and long range crystalline structure. In the gelatinization of starch by heat and shear three different phenomena occur successively: fragmentation of starch granules, hydrogen bond cleavage between starch molecules leading to loss of crystallinity, and partial depolymerisation of the starch molecules. Gelatinization requires sufficient chain mobility that can be provided by heat and mechanical energy in the presence of a plasticizer. The compositional mixture of starch and glycerol after gelatinization leads to the so-called "thermoplastic starch (TPS)" (Li, Luo, Wei, & Huang, 2006). The more difficult it is for the plasticizer to penetrate into the starch amorphous regions – which is affected by plasticizer size and type – the greater the thermal and/or mechanical energy required for the starch chains to gain the sufficient mobility to break down the crystalline structure. The degree of disruption and melting of the crystalline structure of a certain type of starch depends on the plasticizer type, content level and the processing parameters (shear stress, melt viscosity and

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temperature) (Kim & Kim, 2006). Thus, in order to gelatinize starch a plasticizer is required that is able to reduce the T_g of amorphous parts of starch molecules to be able to undergo decrystallization rather than degradation in the presence of heat (Jacobs & Delcour, 1998; Waigh, Kato, et al., 2000). By using water as the plasticizer for starch, the granules will absorb water, swell, lose crystallinity and will arrive at an irreversible state of gelatinized starch. Starch will stay in this condition up until the point that plasticizer is exuded from the physical network of starch molecules. When water is solely used for the plasticization, the material becomes brittle with time at room temperature due to water evaporation (plasticizer exudation) that leads to the so called retrogradation phenomenon. Additionally when water is used as the plasticizer, thermoplastic starch properties are highly affected by the ambient humidity conditions (vanSoest, Benes, deWit, & Vliegenthart, 1996). In order to produce a durable thermoplastic starch, it is necessary to use another plasticizer to hinder starch molecular retrogradation and decrease the humidity dependence. Many different kinds of plasticizers have been studied such as glycerol, glucose, sorbitol, ethylene glycol and amides (Adeodato Vieira, da Silva, dos Santos, & Beppu, 2011; Nashed, Rutgers, & Sopade, 2003; Poutanen & Forssell, 1996). Most of these studies have been carried out for starch prepared films in the food industry. The focus of those articles was mainly the moisture sensitivity and mechanical properties of the films e.g. sorbitol shows superior humidity resistance as compared to glycerol. Glycerol has been the most widely used plasticizer in the industry due to its availability and the final thermoplastic starch mechanical properties (Averous, 2004). Nashed et al. (2003) has reported that glycerol shows strong hydrogen bonding with water which results in its higher water uptake level compared with pure starch. Thus, it might act as an anti-plasticizer in the gelatinization process and increase the water content required for complete gelatinization since it actually decreases the level of available water molecules to penetrate amongst starch chains. Li, Sarazin, and Favis (2008) have shown that the addition of excess water is necessary to reach the gelatinization in the time frame of conventional melt processing. It is believed that water is the main plasticizing agent (Li & Favis, 2010; Li et al., 2008) and the accompanying plasticizer integration with starch molecules is preceded by its water solvation and transfer to starch rich areas. So since water is the most active plasticizer in the gelatinization process due to its low molecular weight and high affinity with starch, the affinity of a second plasticizer with water will influence the gelatinization phenomenon. In literature there is one detailed report on the effect of water/plasticizer ratio on gelatinization and only glycerol has been studied there (Li et al., 2008). They have shown that a high water/plasticizer ratio is required to complete the gelatinization process in the time frame of polymer melt processing. Incorporation of higher molecular weight plasticizers has been shown to increase the gelatinization temperatures (Habeych, Guo, van Soest, der Goot, & Boom, 2009; Perry & Donald, 2002; Tan, Wee, Sopade, & Halley, 2004; van Soest, Bezemer, de Wit, & Vliegenthart, 1996). No matter which plasticizer be used to plasticize starch, it should be able to penetrate into amorphous growth regions of starch and by the plasticizing effect (hydrogen bonding, increasing free volume), increases the molecular mobility. This mobility then allows enthalpically driven transitions happen in the starch and gelatinization begins. It is shown that in this process, aside from starch type, the solvent properties are directly influencing the gelatinization temperature. These properties include viscosity, diffusion rate, molecular weight and hydrogen bonding ability (Tan et al., 2004). In fact the major bonding element for starch granules is hydrogen bonding between them (Perry & Donald, 2000), so as the plasticizer is more efficient in hydrogen bonding, the gelatinization will need less thermal energy uptake and the onset temperature will diminish. On the other hand the availability of the plasticizer i.e. the composition, solution concentration and viscosity which determines the diffusion rate is another factor which is determined by viscosity and molecular weight (Sopade, Halley, & Junming, 2004; Tan et al., 2004).

It has been shown that the gelatinization of starch is facilitated in the presence of mechanical shear during the process through decreasing the required water content (Xue, Yu, Xie, Chen, & Li, 2008). A recent approach developed to study the effect of shear in the gelatinization of starch used a combination of microscopy and a rheoscope rheometer (Yu, Kealy, & Chen, 2006). They were able to successfully study some aspects of the gelatinization phenomenon under shear (Chen, Yu, Kealy, Chen, & Li, 2007). Some authors have also used the evolution of torque in an internal mixer to show the occurrence of gelatinization (Xue et al., 2008). These authors have shown the influence of shear rate on the final equilibrium temperature and torque (after gelatinization) in an internal mixer. In a recent study, Teyssandier, Cassagnau, Gerard, and Mignard (2011) studied the gelatinization of wheat starch in a parallel plate geometry and showed the increase in elastic and loss moduli during the process.

The objective of this study is to determine the mechanism and efficacy of gelatinization in presence of high molecular weight polyols in static and dynamic conditions. This will lead to develop a novel approach to analyze the impact of heat and shear separately on the gelatinization process. The effect of plasticizer molecular weight and structure on the gelatinization phenomenon will be revealed by studying different water/plasticizer ratios for four plasticizer systems in static environments (DSC and optical microscopy). Amongst them are two new plasticizers from polyols family (diglycerol and polyglycerol-3) which are for the first time applied for gelatinization of starch. The investigation of the dynamic gelatinization process by the help of a rheological method for selected plasticizers will determine the effect of shear on gelatinization temperatures. Comparison of static and dynamic methods will differentiate the effect of heat and shear on the gelatinization process which to our knowledge it is for the first time that these effects are being studied separately. This comparison will give us a useful tool to optimize the processing parameters in thermoplastic starch preparation procedure.

2. Experimental

2.1. Materials

The native wheat starch obtained from ADM is composed of 25% amylose and 75% amylopectine. Thermogravimetric analyses showed that the water content of starch granules is around 10%. The glycerol was provided by Labmat with a purity of 99.5% and contained 0.5% water. D-Sorbitol was purchased from Labmat as pure powder. Diglycerol and polyglycerol-3 were produced by Solvay Chemicals. Diglycerol having a min 90% purity was mainly composed of α,α'-diglycrol (84%) and α,β-diglycerol isomers. Polyglycerol-3 mainly includes 35–55% triglycerol, 15–30% of diglycerol and the rest is higher molecular weight polyglycerols resulting in a minimum of 85% of diglycerol, triglycerol and tetraglycerol. The physical properties of the plasticizers are shown in Table 1.

2.2. Sample preparation

To study the gelatinization phenomenon in starch, different mixtures of starch/water/plasticizer were mixed in a mixer and kept at room temperature overnight. The day after, they were again mixed in a mixer for 1–2 min to homogenize the mixture and do the further analyses. Even though water acts as a plasticizer in starch

Table 1
Physical properties of the pure plasticizers.

Property	Unit	Glycerol	Sorbitol	Diglycerol	Polyglycerol	Water
Density	g/cm^3	1.25	1.48	1.27	1.27	1
Glass transition temp.	°C	−65	−9	−54	−45	–
Melting point	°C	17	95	–[a]	–[a]	0
Boiling point	°C	290	296	205	240	100
Solubility parameter (δ_x)	MPa$^{1/2}$	35.76	40.33	29.98	26.9	47.9
$(\delta_{\text{plasticizer}} - \delta_{\text{water}})^2$	MPa	144	57	289	400	–

[a] No melting point was detected in the range of −150 °C to 25 °C.

gelatinization in order to differentiate between water and other plasticizers, plasticizer in this article will refer to glycerol, sorbitol, diglycerol and polyglycerol. The slurry compositions are shown in Table 2. As the slurries are composed of starch/water/plasticizer, the abbreviations for the slurries are the following: SWG# for glycerol, SWSo# for sorbitol, SWD# for diglycerol and SWP# for polyglycerol systems.

2.3. Polarized-light microscopy

In order to visualize the gelatinization phenomenon under static conditions, a Nikon OPTIPHO-2 polarized-light microscope with a Mettler FP82-HT hot stage was used. Using the birefringence properties of anisotropic (crystalline) materials under crossed polarized light, the morphology of starch granules was recorded. In order to provide the same processing conditions for gelatinization as the DSC tests, the samples were heated from 30 to 150 °C at a heating rate of 5 °C min^{-1}. The onset temperature (T_o) was the temperature at which the granules began losing their birefringence and, accordingly the conclusion temperature (T_c) was the point where the birefringence was completely lost.

2.4. Differential scanning calorimetry

In order to obtain the gelatinization temperature of the samples, DSC tests have been conducted on the samples using a differential scanning calorimetry instrument (*DSC Q1000*, *TA instruments*) at a heating rate of 5 °C min^{-1} from 30 to 150 °C with an empty sample pan as the reference. Hermetic pans were used with a sample (starch mixtures) mass of 10–15 mg and were then sealed using a volatile sample sealer accessory. Universal Analysis$^{\text{TM}}$ software was used to determine the onset (T_o), peak (T_p), and conclusion (T_c) temperatures associated with the gelatinization of wheat starch. Onset and conclusion temperatures were the onset and completion of endothermic peaks in DSC curves, respectively, determined by TA Universal Analyses software.

2.5. Rheometry

Rheological characterizations of the slurries were performed in oscillation mode using an AR-2000 stress controlled rheometer from *TA instruments*. The experiments were performed in couette flow geometry with a serrated surface. A stress sweep test was run to define the region of linear viscoelasticity. Then at a shear rate of 6.283 rad/s, a temperature ramp of 5 °C min^{-1} from 30 to 150 °C was conducted on the samples with a controlled oscillating stress. The temperature where the complex viscosity started increasing is defined as the onset temperature and the temperature where it reaches the plateau is considered as the conclusion temperature.

In order to measure the viscosities of the slurries a couette flow geometry of MCR301 rheometer from *Anton Paar* was used. The procedure was a constant shear rate with temperature ramp of 5 °C min^{-1} from 25 °C to 70 °C.

Table 2
Starch/water/plasticizer mixtures compositions: SWG: glycerol, SWSo: sorbitol, SWD: diglycerol and SWP: polyglycerol system.

	Starch (g)	Water (g)	Plasticizer (g)
SWG1	100	30	65
SWG2	100	50	65
SWG3	100	70	65
SWG4	100	100	65
SWG5	100	65	30
SWG6	100	65	50
SWG7	100	65	70
SWG8	100	65	100

2.6. Surface tension measurements

For glycerol and sorbitol, the surface tension values can be found in the literature. The literature does not provide this data for the other two plasticizers, diglycerol and polyglycerol. Since they are viscous liquids; the Wilhelmy plate technique was used. In order to verify the reliability of the results, the surface tension of glycerol was also measured by this method and compared with data reported in the literature.

The surface tension of the above three plasticizers was measured using a Tensiometer (DCAT 21) from Future Digital Sci. Corp. equipped with Wilhelmy plate. In this method a vertical platinum plate, which is roughened to ensure complete wetting, is attached to a tensiometer. Prior to the test the plate was completely wetted by respective sample. The plate was first immersed in the liquid and then pulled upward. At this point the liquid tends to contract the surface area, as it was expanded by the plate, by pulling down the plate. The counteracting force (F) is then measured by the instrument. Surface tension was further calculated through Wilhelmy equation. The surface tension is then related to the solubility parameter by the following equation (Shacklette & Han, 1994):

$$\delta = (14\sigma v^{-1/3})^{1/2} \tag{1}$$

where δ, σ and v are the solubility parameter, surface tension and molar volume, respectively. The results are shown in Section 3.2.

3. Results and discussion

3.1. Optical microscopy

Starch is composed of crystalline parts of amylose and amylopectine and under crossed polarized light the birefringence due to this crystallinity results in a Maltese cross pattern for virgin wheat starch. The gelatinization process disrupts this crystalline structure and leaves an amorphous structure behind which does not show any pattern under polarized light. This method has already been used to study the gelatinization of starch in starch/water/glycerol systems (Derby, Miller, Miller, & Trimbo, 1975; Li et al., 2008; Liu, Charlet, Yelle, & Arul, 2002; Palav & Seetharaman, 2006). In this work we examine the loss of birefringence with temperature for a range of different plasticizers and use this optical microscope technique as evidence for the occurrence of static gelatinization.

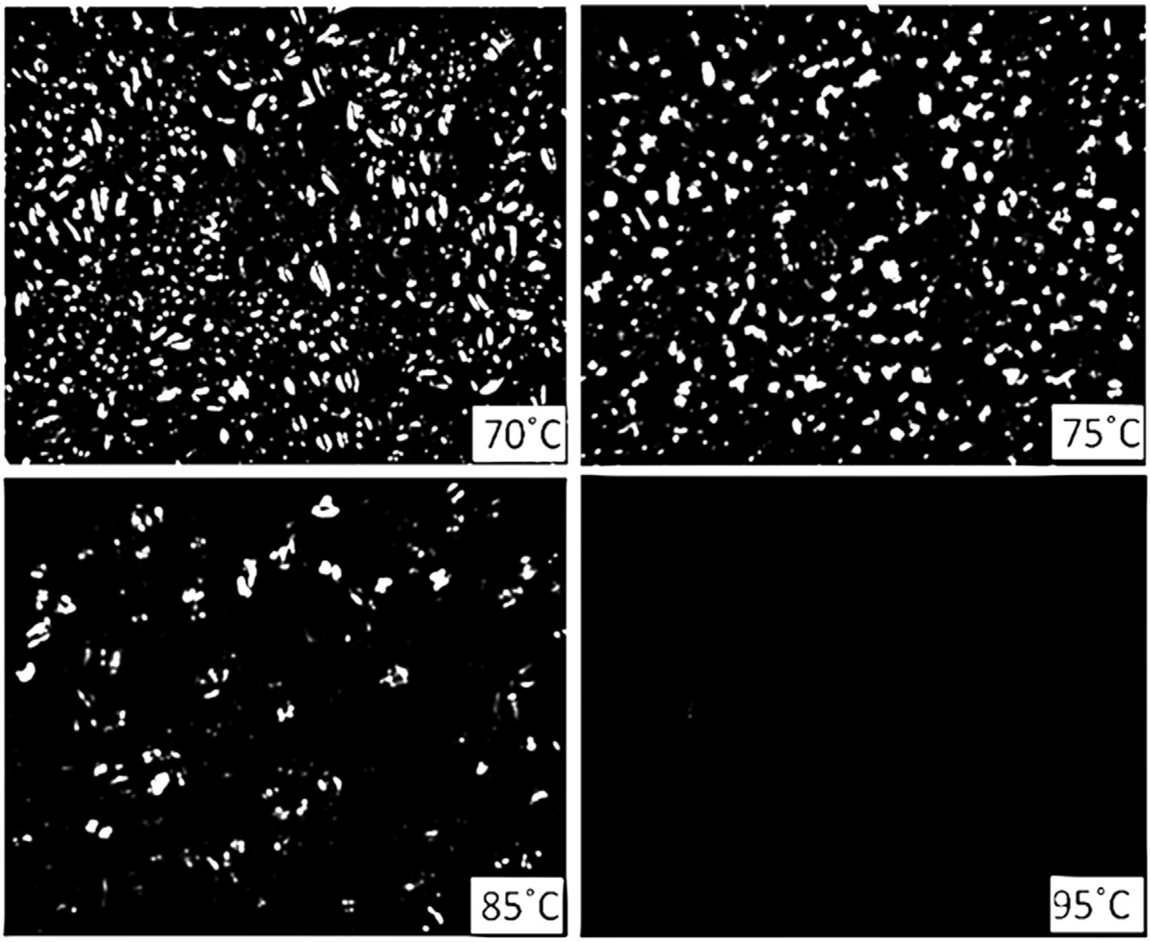

Fig. 1. Optical microscope observation of starch gelatinization when plasticized by water and glycerol (starch/water/glycerol: 100 g/50 g/65 g).

Figs. 1 and 2 demonstrate this gradual loss at different temperatures for glycerol, and polyglycerol at the same water/plasticizer ratios. The onset and conclusion of gelatinization can be clearly observed visually in Figs. 1 and 2. For example in Fig. 2 the birefringence begins to disappear at around 100 °C and finishes at 130 °C which corresponds to the onset and conclusion temperatures obtained by DSC (Section 3.2.). For the 100/50/65 (dry starch/water/plasticizer) samples it can be seen that glycerol and sorbitol show an almost identical behaviour and have the lowest onset and conclusion temperatures, followed by diglycerol and then polyglycerol (Table 3).

3.2. *Differential scanning calorimetry (DSC)*

Gelatinization phenomenon is a first order transition in starch (Zanoni, Schiraldi, & Simonetta, 1995) which produces an endothermic enthalpy peak in DSC thermograms. This DSC analysis allows for the study of samples over a wide range of water/glycerol/dry starch contents. The onset temperature for gelatinization (T_o), the peak temperature (T_P) and the conclusion temperatures (T_c) for diglycerol and sorbitol are listed in Table 4 and are shown graphically for glycerol and polyglycerol in Figs. 3 and 4. The DSC experiments were controlled in two ways which allowed for the observation of increased water and plasticizer content on the gelatinization process. Firstly, the water content in the water/glycerol/starch mixture was modified and the glycerol and starch content was held constant at 65/100 wt%.

Table 3
Optical microscopy visualized gelatinization results.

Starch mixture	T_o (°C)	T_c (°C)
SWG2 (S/W/G: 100 g/50 g/65 g)	71	93
SWSo2 (S/W/So: 100 g/50 g/65 g)	75	95
SWD2 (S/W/D: 100 g/50 g/65 g)	85	120
SWP2 (S/W/P: 100 g/50 g/65 g)	97	130

Table 4
DSC characteristics of starch/water/plasticizer mixtures at various compositions. (a) Sorbitol and (b) diglycerol.

Starch mixture	T_o (°C)	T_P (°C)	T_c (°C)
(a)			
SWSo1 (S/W/So[a]: 100/30/65)	81	85	96
SWSo2 (S/W/So: 100/50/65)	76	80	90
SWSo3 (S/W/So: 100/70/65)	71	75	86
SWSo4 (S/W/So: 100/100/65)	68	72	81
SWSo5 (S/W/So: 100/65/30)	62	68	78
SWSo6 (S/W/So: 100/65/50)	69	74	85
SWSo7 (S/W/So: 100/65/70)	66	71	89
SWSo8 (S/W/So: 100/65/100)	73	78	92
(b)			
SWD1 (S/W/D[b]: 100/30/65)	93	98	123
SWD2 (S/W/D: 100/50/65)	87	91	115
SWD3 (S/W/D: 100/70/65)	81	86	105
SWD4 (S/W/D: 100/100/65)	76	79	97
SWD5 (S/W/D: 100/65/30)	71	76	87
SWD6 (S/W/D: 100/65/50)	77	83	107
SWD7 (S/W/D: 100/65/70)	83	88	109
SWD8 (S/W/D: 100/65/100)	90	95	115

[a] S/W/So: starch/water/sorbitol weights in g.
[b] S/W/D: starch/water/diglycerol weights in g.

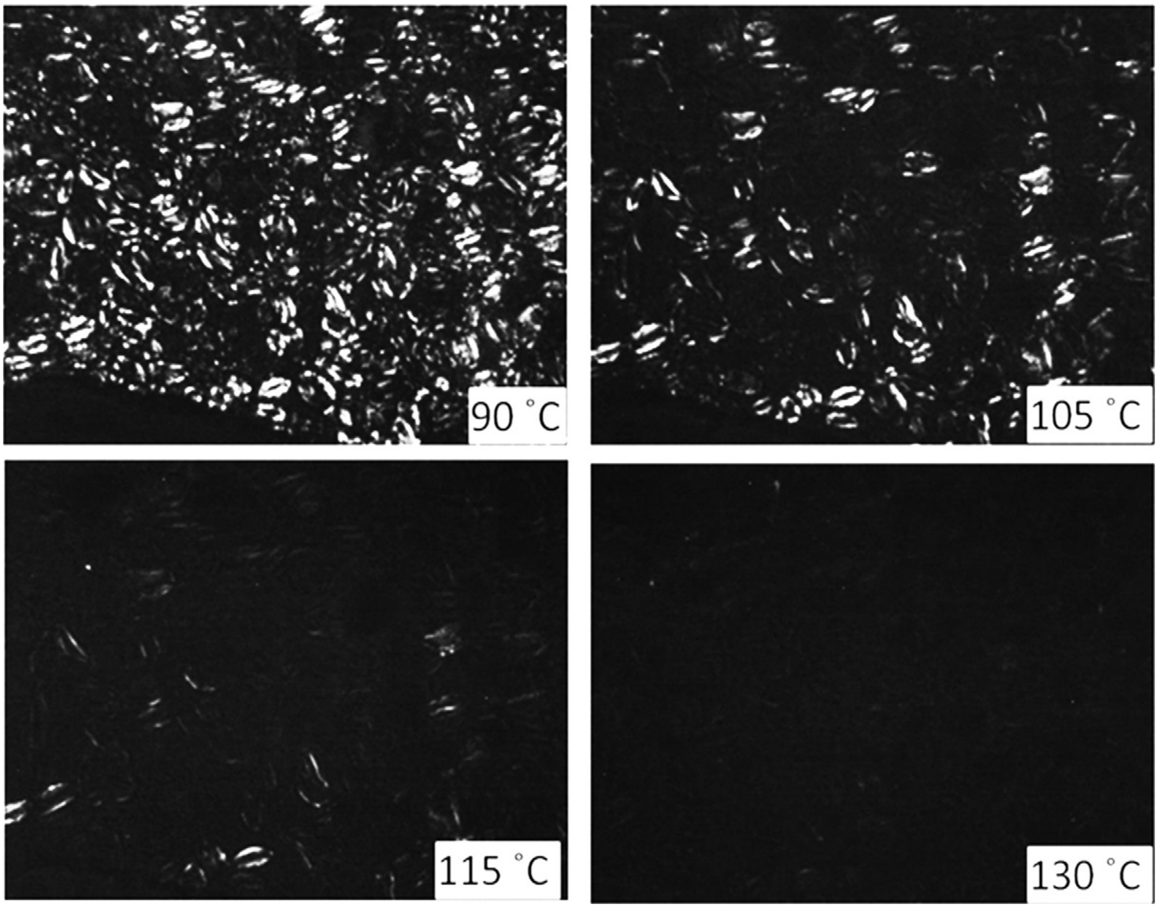

Fig. 2. Optical microscope observation of starch gelatinization when plasticized by water and polyglycerol (starch/water/polyglycerol: 100 g/50 g/65 g).

In the second series of tests the plasticizer content was varied and the water and starch content was held constant at 65/100 wt%.

Table 4 and Figs. 3 and 4 clearly show that over a wide range of starch/plasticizer/water compositions, the gelatinization temperatures increase in the following manner: from glycerol and sorbitol, which show similar behaviours, to diglycerol and finally polyglycerol. The latter two show a considerable increase in gelatinization temperatures. It should be noted that in going from glycerol to diglycerol and polyglycerol there is an important increase in the viscosity of the slurry solution (see Fig. 5).

It is believed that the crystallinity of starch is disrupted in two distinct steps independent of the type of plasticizer used (Perry & Donald, 2000, 2002). First is the plasticization which is mainly controlled by the ingress and diffusion of plasticizer into the amorphous parts of the complex starch granule structure (Antonio,

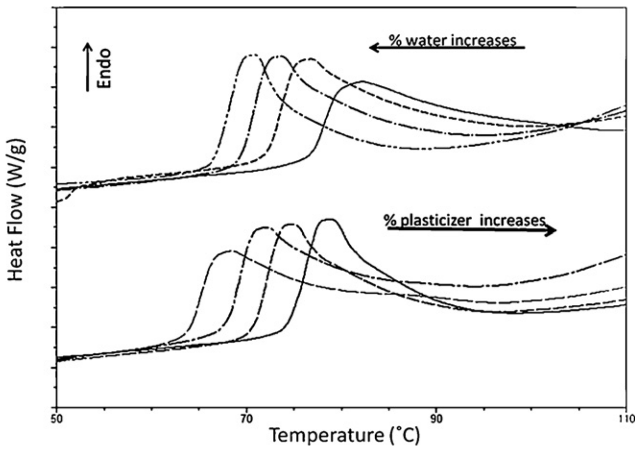

Fig. 3. DSC traces of gelatinization for starch/water/glycerol systems after isothermal treatment at room temperature for 12 h. Upper set, constant starch/glycerol: 100 g/65 g, with increasing water: 30 g (SWG1), 50 g (SWG2), 70 g (SWG3), 100 g (SWG4). Lower row, constant starch/water: 100 g/65 g, with increasing glycerol: 30 g (SWG5), 50 g (SWG6), 70 g (SWG7), and 100 g (SWG8).

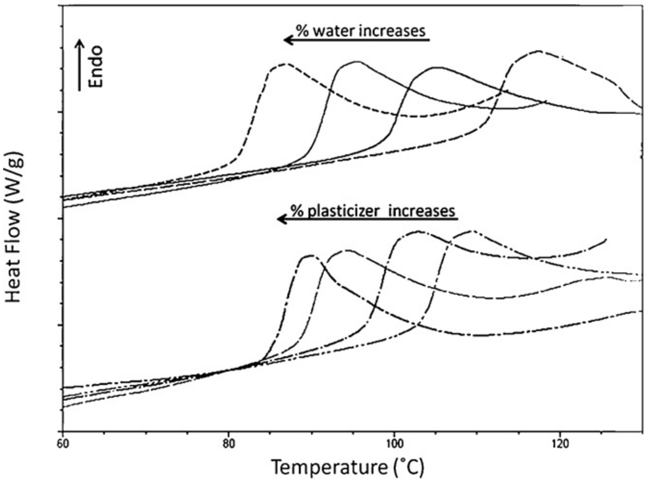

Fig. 4. DSC traces of gelatinization for starch/water/polyglycerol systems after isothermal treatment at room temperature for 12 h. Upper set, constant starch/polyglycerol: 100 g/65 g, with increasing water: 30 g (SWP1), 50 g (SWP2), 70 g (SWP3), 100 g (SWP4). Lower row, constant starch/water: 100 g/65 g, with increasing polyglycerol: 30 g (SWP5), 50 g (SWP6), 70 g (SWP7), and 100 g (SWP8).

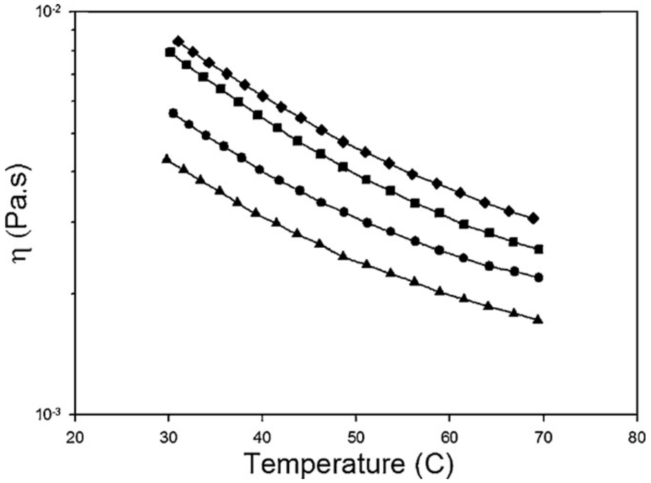

Fig. 5. Viscosity evolution by temperature for plasticizer/water (50/50 wt%) solutions: (▲) glycerol, (●) diglycerol, (■) sorbitol, and (⧫) polyglycerol.

2008). Independent of the type of plasticizer used, this plasticization step has been shown to be an essential precondition for the onset of gelatinization (Perry & Donald, 2002; Tan et al., 2004). During that step the amorphous parts of starch gain a certain degree of freedom and molecular activity. In the second step, this mobility ascends to a level such that helix-coil irreversible transition initiates and the crystalline structure begins to disrupt; that is called gelatinization (second step). During gelatinization, starch–starch hydrogen bonds should be disrupted and at the same time starch–solvent hydrogen bonding should be built (Antonio, 2008; Tan et al., 2004).

The dynamics of the plasticization process discussed above will have an influence on the gelatinization temperature. Considering that the most important structural element building the starch crystalline structure is the starch–starch hydrogen bonding (Antonio, 2008), by increasing the hydrogen bonding capacity of the plasticizers, the lamellar plasticization can be reached at lower temperatures (Perry & Donald, 2000; Waigh, Gidley, Komanshek, & Donald, 2000). Tan et al. (2004) recently showed that in addition to the hydrogen bonding ability of plasticizers, the solvent transport ability in granules of starch is of great importance in determining the gelatinization temperature. This ability is determined by parameters like molecular weight, viscosity and diffusion rate (Perry & Donald, 2000; Tan et al., 2004; Ternstrom, Sjostrand, Aly, & Jernqvist, 1996). The amount of energy or molecular mobility which a certain type of plasticizer can provide to starch is another factor. It is shown that polyols cannot introduce the same level of degree of freedom that water can give to polysaccharides (Kilburn, Claude, Schweizer, Alam, & Ubbink, 2005). Thus even if the ingression has reached higher levels (e.g. by long time solution conditioning), the amount of energy that is needed for the amorphous parts to reach the max level of mobility is increased in presence of polyol plasticizers as compared to water (Perry & Donald, 2002). On the other hand water activity can be retarded in the presence of polyols due to their high affinity with water in such a way that over a certain ratio of plasticizer/water, the plasticizers compete with starch in bonding with water molecules (Godbillot, Dole, Joly, Roge, & Mathlouthi, 2006; Mali, Sakanaka, Yamashita, & Grossmann, 2005). It is also shown that the ingress rate of plasticizers in polysaccharides is greatly dependent upon the molecular weight of plasticizers (Smits, Kruiskamp, van Soest, & Vliegenthart, 2003) and the water concentration in water/polyol mixtures (Ternstrom et al., 1996). It is interesting to note that despite the higher viscosity of sorbitol as compared to glycerol, these two plasticizers show a virtually identical set of gelatinization temperatures. It has been already shown that a higher molecular weight of plasticizer would have a tendency to increase the gelatinization temperature according to free-volume theory (Shacklette & Han, 1994). On the other hand the density of hydroxyl groups can also affect the hydrogen bonding ability of the plasticizers (Perry & Donald, 2000). For example in the case of sorbitol (M_w: 182 g mol^{-1}) and glycerol (M_w: 92 g mol^{-1}), although sorbitol has a higher molecular weight, it has the same hydroxyl group density as glycerol. Due to the various conformational structures (Lerbret et al., 2009) that sorbitol can adopt, it has been shown to have a higher level of interaction with starch than glycerol (Garcia, Martino, & Zaritzky, 2000; Mali et al., 2005). This high level of interaction likely counterbalances any plasticization retarding effect due to the higher viscosity or molecular weight of the sorbitol and it demonstrates onset and conclusion gelatinization temperatures similar to glycerol.

In the case of diglycerol (M_w: 166 g mol^{-1}) it has a similar molecular weight to sorbitol and, despite its lower slurry viscosity than sorbitol (Fig. 5), it shows higher onset gelatinization temperatures. This can be attributed to the lower density of hydroxyl bonds which affects its plasticizing ability, hence the gelatinization temperature increases (Perry & Donald, 2000). For the case of polyglycerol, the molecular weight ($M_w \approx 250$ g mol^{-1}) as well as the slurry viscosity is high and it has a hydroxyl group density which is low as compared to the other plasticizers. All these factors combined contribute to the significantly higher gelatinization temperatures observed for polyglycerol.

For glycerol, sorbitol, diglycerol and polyglycerol, when the plasticizer/starch content is held constant at 65/100 wt% and the water content is increased, the gelatinization peaks shift to lower temperatures (Table 4). This is quite expected because of the increasing water content and the better efficacy of water as a plasticizer of starch. It is also supported by the fact that increased water content decreases the slurry viscosity and improves the diffusion rate into the starch granules. Conversely, when the water mass is held constant and the plasticizer content is increased, the gelatinization temperature increases for glycerol, sorbitol and diglycerol as expected. Polyglycerol, however, provides a very different behaviour. Fig. 4 shows that when the water/starch ratio is held constant and the polyglycerol plasticizer content is increased, the gelatinization temperatures for this plasticizer are moved to lower temperatures.

In order to further understand this anomalous behaviour of polyglycerol, we estimated the solubility parameters and the main enthalpic term for water and the various plasticizers (Table 1). It can be seen that the enthalpic tendency for mixing for polyglycerol is the least amongst the various plasticizers. Thus, polyglycerol has the least tendency for solubilization in water and sorbitol has the highest. As already mentioned, water is a key factor in plasticizing starch. In order to test this hypothesis, the slurry temperature was increased for the polyglycerol sample and under those conditions, the normal trend of onset temperature augmentation is observed (Fig. 6) thus confirming the solubility issue with polyglycerol.

Irrespective of the type of the plasticizer, initiation of gelatinization requires a certain level of plasticization of starch molecules. Any parameter influencing (a) the efficacy of plasticizer penetration into starch granules and disruption of the existing crystalline structure, (b) the water/plasticizer-starch hydrogen bonding or water/plasticizer availability for starch and (c) the water/plasticizer ingress rate will effect the required thermal energy required to disrupt the crystalline structure and consequently will effect gelatinization temperatures. It should be noted that a number of these factors determining the gelatinization temperature are interrelated and it is difficult to isolate the clear role of each.

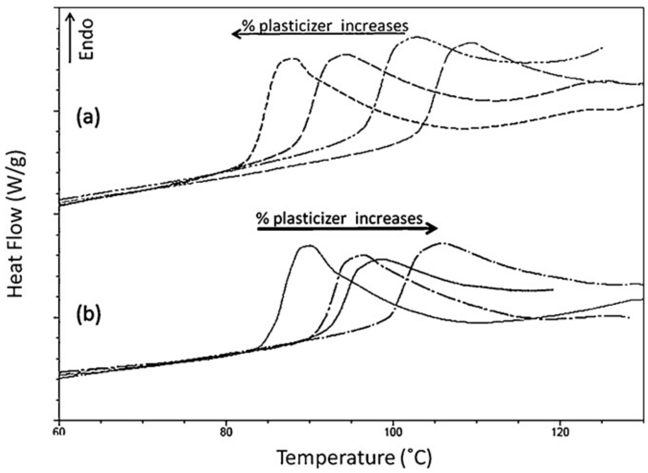

Fig. 6. DSC traces of gelatinization for wheat starch/water/polyglycerol systems after isothermal treatment: (a) at room temperature for 12 h and (b) at 50 °C for 12 h. Constant starch/water: 100 g/65 g, with increasing polyglycerol: 30 g (SWP5), 50 g (SWP6), 70 g (SWP7), and 100 g (SWP8).

3.3. Effect of shear on gelatinization

The gelatinization of starch results in the transformation of the plasticizer/water/starch mixture from a suspension of starch particles in low molecular weight fluids to a gel-like fluid whose characteristics are dominated by the high molecular weight starch molecules. Gelatinized starch shows a pronounced shear thinning behaviour over the whole frequency sweep range (Li & Favis, 2010). This behaviour is attributed to the existence of a hydrogen bonding network between plasticizer and starch molecules as well as the physical network of starch molecules (macromolecular entanglements) or remaining crystallinity in starch molecules (Rodriguez-Gonzalez, Ramsay, & Favis, 2004). As mentioned earlier, gelatinization can proceed under static conditions in presence of heat and a plasticizer, but in conventional polymer processing equipment such as extrusion, the gelatinization is conducted under dynamic conditions where different shear fields are engaged (Huneault & Li, 2007; Rodriguez-Gonzalez, Ramsay, & Favis, 2003; Taguet, Huneault, & Favis, 2009; Willett & Shogren, 2002). This part examines the potential of tracking the real effect of shear in the gelatinization process using a controlled rheological technique outlined in Section 2.

Figs. 7 and 8 show the rheological curves of viscosity evolution with temperature for different wheat starch/water/plasticizer ratios. The same approach was used as in the static work reported above: in one case the composition of plasticizer/starch is held constant and water content is increased (Figs. 7(a) and 8(a)); and in the other case the composition of starch/water is held constant and plasticizer content is increased (Figs. 7(b) and 8(b)). The curves demonstrate a sharp increase in complex viscosity of the mixture

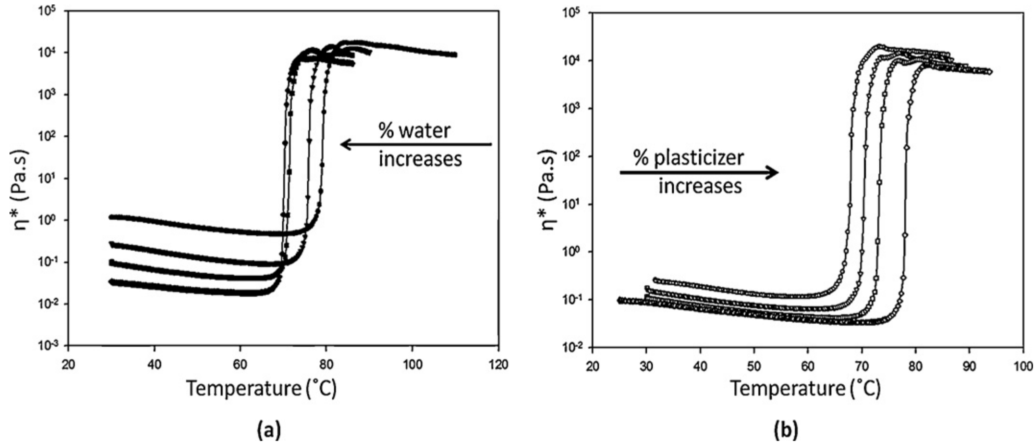

Fig. 7. Rheological traces of gelatinization for starch/water/glycerol (S/W/G) systems at different compositions: (a) constant starch/glycerol: 100 g/65 g, with increasing water: 30 g (SWG1), 50 g (SWG2), 70 g (SWG3), 100 g (SWG4), (b) constant starch/water: 100 g/65 g, with increasing glycerol: 30 g (SWG5), 50 g (SWG6), 70 g (SWG7), and 100 g (SWG8).

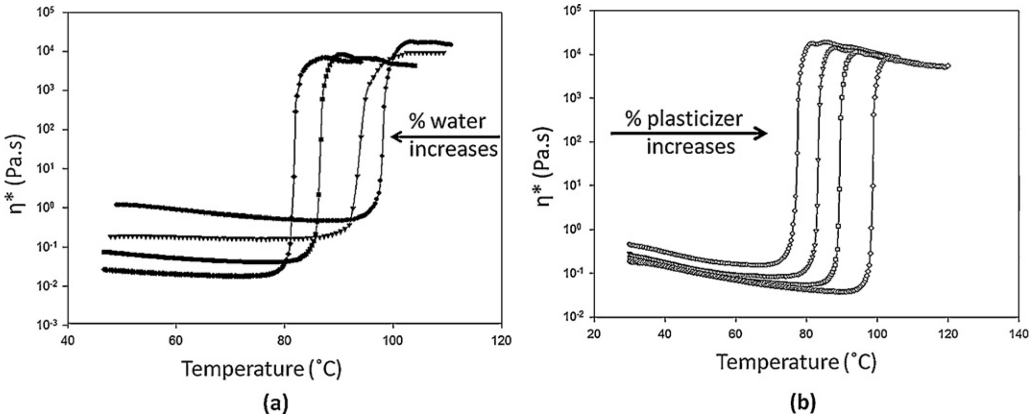

Fig. 8. Rheological traces of gelatinization for wheat starch/water/diglycerol (S/W/D) systems at different compositions: (a) constant starch/diglycerol: 100 g/65 g, with increasing water: 30 g (SWD1), 50 g (SWD2), 70 g (SWD3), 100 g (SWD4), (b) constant starch/water: 100 g/65 g, with increasing diglycerol: 30 g (SWD5), 50 g (SWD6), 70 g (SWD7), and 100 g (SWD8).

Table 5
Comparison of onset and conclusion gelatinization temperatures from DSC and rheology for glycerol.

	T_o (DSC) (°C)	T_o (Rheology) (°C)	T_c (DSC) (°C)	T_c (Rheology) (°C)
SWG1 (S/W/G: 100/30/65) [a,b]	77	77	101	83
SWG2 (S/W/G: 100/50/65)[b]	72.4	74	91	82.9
SWG3 (S/W/G: 100/70/65)[b]	69.4	70	88	79
SWG4 (S/W/G: 100/100/65)[b]	66.7	67.4	83	74
SWG5 (S/W/G: 100/65/30)[c]	64.1	64.8	80.9	76
SWG6 (S/W/G: 100/65/50)[c]	68	68.3	85.6	77
SWG7 (S/W/G: 100/65/70)[c]	70.9	71	89.5	79
SWG8 (S/W/G: 100/65/100)[c]	74.7	76	91.5	84

[a] S/W/G: Starch/water/glycerol weights in g.

[b] Plasticizer weight constant.

[c] Water weight constant.

Table 6
Comparison of onset and conclusion gelatinization temperatures from DSC and rheology for sorbitol.

	T_o (DSC) (°C)	T_o (Rheology) (°C)	T_c (DSC) (°C)	T_c (Rheology) (°C)
SWSo1 (S/W/So: 100/30/65)[a,b]	81	80	96	88
SWSo2 (S/W/So: 100/50/65)[b]	76	77	90	79
SWSo3 (S/W/So: 100/70/65)[b]	71	70	86	75
SWS4 (S/W/So: 100/100/65)[b]	68	67	81	72
SWSo5 (S/W/So: 100/65/30)[c]	62	60	78	68
SWSo6 (S/W/So: 100/65/50)[c]	69	70	85	76
SWSo7 (S/W/So: 100/65/70)[c]	66	68	89	79
SWSo8 (S/W/So: 100/65/100)[c]	73	74	92	81

[a] S/W/G: Starch/water/glycerol weights in g.

[b] Plasticizer weight constant.

[c] Water weight constant.

Table 7
Comparison of onset and conclusion gelatinization temperatures from DSC and rheology for diglycerol.

	T_o (DSC) (°C)	T_o (Rheology) (°C)	T_c (DSC) (°C)	T_c (Rheology) (°C)
SWD1 (S/W/D: 100/30/65)[a,b]	93	92	123	102
SWD2 (S/W/D: 100/50/65)[b]	87	88	115	103
SWD3 (S/W/D: 100/70/65)[b]	81	82	105	91
SWD4 (S/W/D: 100/100/65)[b]	76	77	97	88
SWD5 (S/W/D: 100/65/30)[c]	71	71	87	81
SWD6 (S/W/D: 100/65/50)[c]	77	78	107	88
SWD7 (S/W/D: 100/65/70)[c]	83	84	109	94
SWD8 (S/W/D: 100/65/100)[c]	90	92	115	102

[a] S/W/G: Starch/water/glycerol weights in g.

[b] Plasticizer weight constant.

[c] Water weight constant.

during gelatinization. Both increasing the water content series and increasing the plasticizer content series show similar trends as that observed in the static DSC tests (Fig. 3) and the polarized light microscope observations i.e. the gelatinization temperature decreases when increasing the water/starch ratio and the gelatinization temperature increases when the plasticizer/starch ratio increases.

It is important to note that some very important differences are observed under shear as compared to static conditions. Tables 5–7 shows the comparison between the onset and conclusion temperatures of the different compositions obtained by rheometry and the corresponding temperatures from the DSC for each plasticizer. It is observed that the initiation temperatures for gelatinization from both static (DSC) and dynamic (rheological) techniques closely correspond to each other and shear has virtually no effect on the onset temperature of gelatinization. However, the conclusion temperatures drop considerably under shear conditions as compared to the static DSC results.

As discussed in the previous section, in order for gelatinization to occur, the amorphous parts of starch require a certain level of energy in order to gain enough mobility to be able to begin disruption of helix–helix interactions in crystalline parts. This energy is partly obtained by plasticizer ingress into starch structure and completed afterwards by thermal energy input. Shear would be expected to have a particular influence on plasticizer ingress rates. Note however that the onset temperature for gelatinization is likely related to the onset of gelatinization of the most accessible layer of starch granule. Following that, plasticization–gelatinization takes place in other parts of the starch granule. The plasticizer ingression to the amorphous parts continues up until the peak gelatinization temperatures (Donald, Kato, Perry, & Weigh, 2001). These results suggest that ingress rates have little influence on the onset temperature, but are critical in determining the conclusion temperature. These results highlight the important consideration that will need to be given to the effect of residence time on gelatinization in extrusion processes where the residence time is normally very limited (<2 min). The conclusion temperature of gelatinization can be significantly influenced by mixing conditions. Consequently, the initiation temperature for gelatinization of starch appears to be controlled by the efficacy of the plasticizer in plasticizing the amorphous parts of starch and shear has virtually no effect on it. The conclusion temperature, on the other hand, demonstrates the characteristics of a parameter which is more kinetically controlled. Improvements to the mixing efficacy (i.e. plasticizer ingress into starch granules) will assist the disintegration of starch crystals and the principal effect will be a drop in the conclusion temperature.

4. Conclusions

In this work a detailed study of the gelatinization regime at various starch/water/plasticizer ratios has been conducted for four different plasticizers. Optical microscopy is used to confirm the occurrence of gelatinization for all the plasticizers during which the starch granules lose their birefringence. Static gelatinization has also been investigated with DSC tests. The onset and conclusion gelatinization temperatures for the different plasticizers increase in the following order:

$$\text{Glycerol} \approx \text{Sorbitol} \ll \text{Diglycerol} < \text{Polyglycerol}$$

Glycerol and sorbitol have very similar gelatinization temperatures. The ascending gelatinization temperature from glycerol to diglycerol and polyglycerol was attributed to the viscosity and molecular weight increase and hydroxyl bond density diminution of the latter two plasticizers. Comparing the gelatinization temperatures of sorbitol and diglycerol, with similar molecular weights, the former is shown to have a higher efficacy in starch gelatinization than diglycerol. This is most likely due to the higher hydroxyl group density of sorbitol and its higher level of interaction with water. All of the above plasticizers demonstrate a lower gelatinization temperature when the water/starch ratio is increased, due to the efficacy of water in plasticizing starch. Conversely, when the plasticizer/starch ratio is increased, the gelatinization temperature increases for glycerol, sorbitol and diglycerol. Polyglycerol shows an anomalous behaviour and the gelatinization temperature is found to drop when increasing the plasticizer/starch ratio. This was found to be the result of the limited water solubility of polyglycerol. When the slurry temperature for the polyglcerol suspension is increased, the trend of increasing gelatinization temperature with increasing plasticizer/starch ratio is observed.

The effect of shear on gelatinization is examined through a detailed rheological investigation conducted on the glycerol, diglycerol and sorbitol slurries. It is found that the onset gelatinization temperatures for glycerol, sorbitol and diglycerol are independent of the applied shear and are identical to that observed under static conditions. The conclusion temperature, on the other hand, drops considerably upon application of shear as compared to the static data. It demonstrates the characteristics of a parameter which is more kinetically controlled and which could be significantly influenced by mixing conditions.

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