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Rheological properties of thermoplastic starch studied by multipass rheometer

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ABSTRACT

The rheological properties of thermoplastic starch (TPS) melt were investigated using the new multipass rheometer (MPR). This rheometer consists of two servo-hydraulically driven pistons and a fully closed barrel, enabling pressurisation of sample and preventing moisture loss during the process. The starch samples (with different plasticiser contents, 70–110%, and at different glycerol/water ratio, 1:4, 2:3, and 3:2) were first well transformed into TPS in MPR and then tested at different temperatures (90, 110 and 130 °C). The TPS behaved as a shear-thinning material, and the power-law model was used to describe its rheological behaviour. The combination of glycerol and water had the greatest influence on the power-law index *n* while temperature had little influence. By mastercurve study, it was shown that the higher the glycerol/water ratio, the stronger the shear-thinning behaviour was. This was explained by interaction between starch and plasticiser and different structural characteristics at different conditions.

1. Introduction

Due to the environmental concerns and the shortage of oil, the use of starch resources in non-food applications has experienced considerable development in the past decades in order to find substitutes to petroleum-based plastics. Using conventional polymer processing techniques such as extrusion, raw starch can be converted into a homogeneous molten state (thermoplastic starch, TPS) with the presence of low content of plasticisers such as water and glycerol. The TPS batch master can be produced into various products such as sheets/films, foams and other specific shapes by ways of extrusion, injection/compression moulding, and so on (Liu, Xie, Yu, Chen, & Li, 2009). As a result, the understanding of the rheological behaviour of TPS is highly important in determining optimal processing conditions and better controlling the quality of starch-based products.

The rheology of TPS has been widely investigated before. However, since TPS usually contains water, traditional open rheometry (such as rotational) is not appropriate for TPS due to the loss of water during measurement. Instead, most research has been focused on the use of extruder-fed slit/capillary rheometry in the study of rheological properties of TPS. In some studies (Lai & Kokini, 1990; Xie et al., 2009), raw starch was first plasticised using a twin-screw extruder; then, a single-screw extruder equipped with a slit/capillary die was used to evaluate the rheological properties of plasticised starch during the second run. Other studies (Della Valle, Colonna, Patria, & Vergnes, 1996; Martin, Averous, & Della Valle, 2003) involved using a slit/capillary die which directly installed at the head of the twin-screw extruder to carry out online rheological measurement of starch for a single run. From the past reports (Cervone & Harper, 1978; Fletcher, McMaster, Richmond, & Smith, 1985; Padmanabhan & Bhattacharya, 1991; Senouci & Smith, 1988; Vergnes & Villemaire, 1987; Willett, Jasberg, & Swanson, 1995), it has been found that thermoplastic behaviour of low-hydrated molten starch normally depends on various processing factors such as temperature, moisture (and plasticiser) content, specific mechanical energy (SME), screw speed, and even extruder barrel pressure; based on the basic shear-thinning model ($\eta = K\dot{\gamma}^{n-1}$), various modified rheological models relating to these effects have been proposed to describe the rheological properties of TPS.

Though some past studies of rheological properties of TPS considered the effect of starch transformation or molecular degradation during extrusion processing (Della Valle, Boché, Colonna, & Vergnes, 1995; Della Valle, Colonna, Patria, & Vergnes, 1996; Lai & Kokini, 1990; Martin et al., 2003; Willett, Millard, & Jasberg, 1997), a very recent finding (Liu, Halley, & Gilbert, 2010) revealed that extrusion degradation process only cause the size distribution of starch molecules to narrow and converge toward a maximum stable size due to both the selective scission and the maximum stable size concept. This means starch melt may achieve a stable structural (and thus rheological) state under processing with shear and heat

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Abbreviations: TPS, thermoplastic starch; MPR, multipass rheometer.

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treatments. If the effect of structural changes or degree of transformation can be eliminated, the effects of other parameters such as sample formulation and testing conditions on the TPS rheology could be more clearly demonstrated.

Recently, a new multipass rheometer (MPR) has been developed and used in the rheological measurements of liquids and polymer melts (Lee & Mackley, 2001; Mackley, Marshall, & Smeulders, 1995; Ranganathan, Mackley, & Spitteler, 1999). This rheometer consists of two servo-hydraulically driven pistons that can be moved together or separately. When the material is fed into the rheometer, one piston will be moved towards the other until desired pressure is achieved. When the hydrostatic pressure is set, the two pistons were then moved synchronously during testing so that their distance remains constant. Compared to other conventional rheometers, MPR has some advantages such as the requirement of only a small amount (~20 g) of sample, the pressurisation of sample, and the fully closed and sealed barrels. These allow MPR to be a suitable tool to measure the rheological properties of TPS.

In this work, MPR was applied to study the rheological properties of TPS for the first time. Water and glycerol were used as plasticisers to prepare TPS as they are most commonly used in practical production. The preparation of TPS was carried out in the MPR as well and a stable rheological state was achieved before any meaningful measurements. The effects of temperature, shear rate, plasticiser content, and glycerol/water ratio were investigated. The rheological behaviour of starch melt will be modelled. The effects of plasticiser content and glycerol/water ratio will be discussed in detail.

2. Experimental

2.1. Materials and samples preparation

Waxy maize starch (Mazaca 3401X) was supplied by Penford Australia Ltd. (Lane Cove, NSW, Australia). The original moisture content of waxy maize starch was 16.4%, and the amylose content was 3.4% as determined in our previous study (Tan, Flanagan, Halley, Whittaker, & Gidley, 2007). Glycerol (analytical grade at 99.5% purity) was supplied by Ajax Finechem Pty Ltd. (Australia). Milli-Q water was used in all instances. Before use, waxy maize starch was well blended with specific amounts of water and glycerol to achieve different total plasticiser contents (70%, 90%, and 110%, based on dry starch) and different glycerol/water ratios (1:4, 2:3, and 3:2). The blended samples were then stored in sealed bags for at least 3 days for equilibrium.

2.2. Differential scanning calorimetry (DSC)

A PerkinElmer Diamond differential scanning calorimeter (DSC) with an internal coolant (Intercooler IP) and nitrogen purge gas was used to determine the phase transition temperature range of the prepared samples. Melting point and enthalpies of indium and zinc were used for temperature and heat capacity calibration. The samples (about 7 mg, dry basis) were accurately weighed in high-pressure stainless steel pans (PerkinElmer No.: B0182901) for DSC measurements. The slow heating rate of 5 °C/min was used to minimise any temperature lag due to the large mass of the steel pan (Yu & Christie, 2001). Samples were subjected to a heating scan from 30 °C to 200 °C at 5 °C/min. Each run was repeated at least twice to ensure the repetition of the results.

2.3. Multipass rheometer (MPR)

The MPR is schematically depicted in Fig. 1. It is made of stainless steel and consists of a top and a bottom barrel through which two servo-hydraulically driven pistons enter the rheometer assembly with a capillary test section positioned between the barrels. Pressure transducers and temperature thermocouples located in the top and bottom barrel sections are used to monitor the system temperature and pressure. A capillary with appropriate dimensions is chosen for a measurement. Temperature of the barrels and capillary is controlled by the cooling/heating jackets connecting to an oil bath.

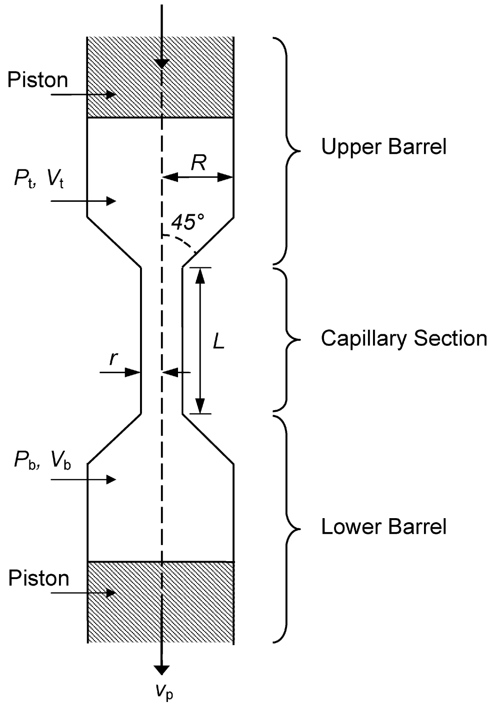

Fig. 1. Schematically representation of multipass rheometer. The barrel/piston radius (R) was 5 mm; the capillary radius (r) used was 2 mm; the capillary lengths (L) used were 1 mm, 10 mm, and 40 mm; P_t and P_b represent the pressure in the top and bottom barrel, respectively; V_t and V_b represent the volume flow rate in the top and bottom barrel, respectively.

After sample is introduced into the MPR, one piston will be moved toward the other until a specific hydrostatic pressure is achieved. The two pistons are then synchronously driven such that their separation remains constant. In this study, "multipass steady" mode was used, which means the pistons advance at constant velocity for a given time, yielding steady shear data. The piston position is then held constant for a set dwell time (1 s) and then the piston motion is reversed. In this way a multitude of successive steady flow measurements can be made on the same test fluid.

2.4. Sample processing and rheological measurements by MPR

Since MPR requires only a small amount of sample and can completely seal its inner space, the preparation of TPS was also carried out using MPR in this study. Starch sample (previously blended with glycerol and water, ~20 g) was introduced into the MPR and then sealed by closing the barrel and moving the piston. The sample was heated to specific temperature (see Table 1) and kept at that temperature for 5 min. Then, one piston was moved again to achieve a hydrostatic pressure of about 0.4 MPa. A multipass steady run was carried out at piston speed of 10 mm/s and dwell time of 1 s. The change of apparent viscosity of the sample with time could be monitored by the MPR software (Fig. 2). When the viscosity reach a stable value, it could be considered the sample achieve a stable state and is ready for rheological tests.

The sample temperature was then set at different values (90, 110, and 130 °C, ±1 °C) for rheological measurements. One pis-

Table 1
DSC results of different starch samples and the temperatures used for their processing.

Total plasticiser content (%)	Glycerol/water ratio	Gelatinisation temperature range (°C)	Temperature for sample processing (°C)
70	1:4	73.9–118.1	130
70	2:3	82.7–130.1	131
70	3:2	87.4–158.5	160
90	3:2	87.4–131.0	131
110	3:2	87.3–120.8	130

ton was moved to achieve a hydrostatic pressure of about 0.4 MPa again. Different piston speeds (v_p, 2–80 mm/s) were used for obtaining the result at a wide range of shear rates. The dwell time was 1 s for all the piston speeds. At each piston speed, about 10 circles were carried for a reliable result. The signals such as time, top or bottom piston position, and top (P_t) or bottom (P_b) barrel pressure could be obtained from the MPR. The result of the changes of differential pressure and piston position with time during a multipass steady run could be obtained by the MPR software. From this result, mean differential pressure (ΔP) could be calculated at certain piston speed. In this study, capillaries with different lengths (1, 10, and 40 mm) and of 4 mm diameter were used for all the samples. As a result, Bagley correction could be applied (Bagley, 1957). The corrected shear stress was obtained from:

$$\sigma_w = \frac{\Delta P}{2\left(L/r + e\right)} \tag{1}$$

where L the length (m) of the capillary, r the radius (m) of the capillary, and e the intercept with x-axis when plotting ΔP as a function of L/r.

Since TPS is a non-Newtonian fluid (Della Valle et al., 1996; Lai & Kokini, 1990; Martin et al., 2003; Xie et al., 2009), Rabinowitsch correction was applied when calculating the shear rate (Klyosov, 2007):

$$\dot{\gamma}_w = \dot{\gamma}_{app}\left(\frac{3}{4} + \frac{1}{4}\frac{d \ln Q}{d \ln \sigma_w}\right) \tag{2}$$

where Q is the volume flow rate (m^3/s) and equal to $\pi R^2 v_p$ with R the piston radius (0.005 m).

The viscosity could then be calculated:

$$\eta = \sigma_w / \dot{\gamma}_w \tag{3}$$

The mass of the samples before and after the processing and rheological measurements was determined. No significant variation of the mass was observed, which indicates that the moisture was constant in MPR.

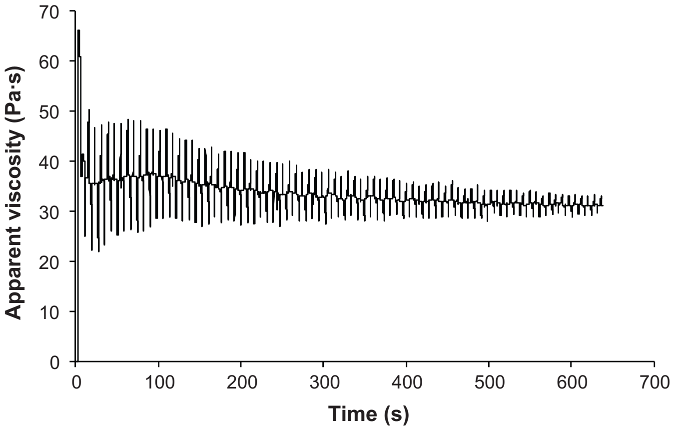

Fig. 2. A typical result of processing of starch by MPR (total plasticiser content = 90%; glycerol/water ratio = 3:2; temperature at 130 °C).

3. Results and discussion

3.1. *Sample processing*

While some past reports on the rheological properties of molten starch took into account the effect of starch transformation or molecular degradation during extrusion processing (Della Valle et al., 1995; Della Valle et al., 1996; Lai & Kokini, 1990; Martin et al., 2003; Willett et al., 1997), this work aims at determining the rheological properties of fully transformed starch without any effect related to further structural and molecular changes. This is based on a very recent study (Liu et al., 2010) that the molecular degradation of waxy maize starch under shear stress during extrusion only cause the size distribution of starch molecules to narrow and converge toward a maximum stable size within a limited time. As a result, it was possible to prepare fully developed TPS with stable rheological properties under shear stress in this study.

To achieve this, both heat and shear treatment were applied in MPR for processing raw starch into TPS. The DSC measurements were carried out to understand the temperature range for the phase transition of the samples, and the results are shown in Table 1. Based on the DSC results, the temperatures for processing different samples are chosen, which were at least the conclusion temperatures of the phase transition. For some samples, the processing temperature was higher than the conclusion temperature of phase transition; however, no thermal decomposition would happen based on a previous study (Liu, Yu, Liu, Chen, & Li, 2009). After the sample temperature reached the desired value, a multipass run was carried out to enforce shear treatment for facilitating phase transition and to ensure the sample to achieve a homogeneous and stable molten state. Fig. 2 shows a typical result of sample processing by MPR. It can be seen that there was much noise of the apparent viscosity at the start, but the noise gradually diminished with time. Besides, the average value of apparent viscosity first increased to a small extent, and then gradually decreased to a stable level. These changes could reflect the transformation and molecular degradation of starch during processing in MPR. After 500 s, the apparent viscosity was considered to be constant; thus the rheological properties of TPS were regarded to be in stable state and will not change with further shear treatment. For each sample, such processing was carried out to ensure the apparent viscosity to reach a stable state before any rheological measurements.

3.2. *Effect of total plasticiser content*

Fig. 3 shows the effect of total plasticiser content on the rheological properties of TPS at different temperatures (90, 110, and 130 °C). The glycerol/water was kept at 3:2. It can be seen that, in all cases, a linear line can be used to describe the relationship between viscosity and shear rate in double-logarithmic plot, indicating a strong power-law dependence of viscosity on shear rate for TPS. This power-law behaviour will be discussed later. Besides, a similar shear-thinning behaviour can be observed in all cases, though higher temperature or total plasticiser content would shift viscosity to a lower level.

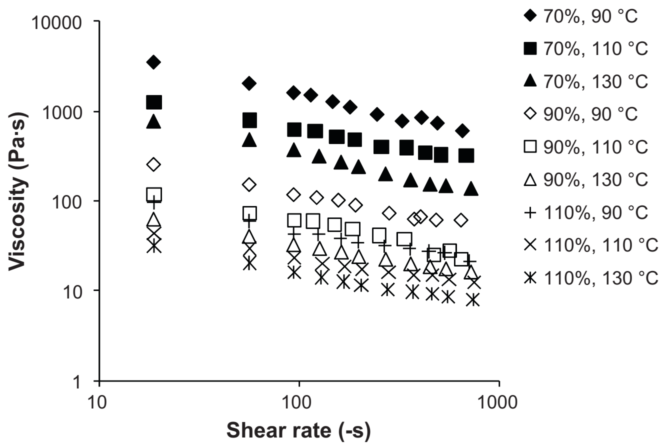

Fig. 3. The effect of total plasticiser content on the rheological properties of waxy starch melt at different temperatures (90, 110, 130 °C). Glycerol/water ratio = 3:2.

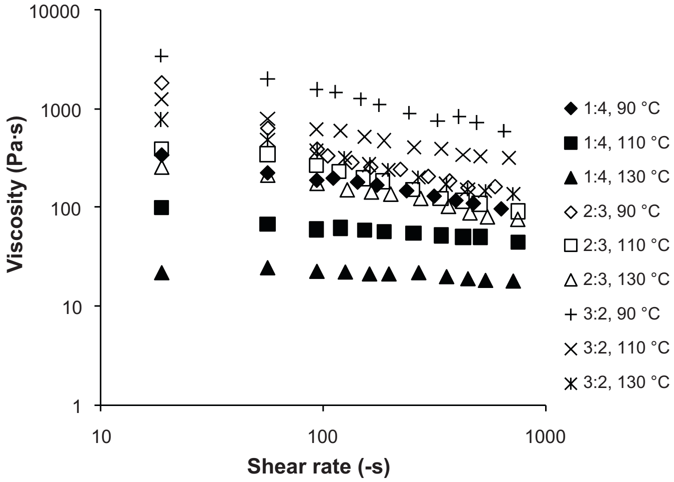

Fig. 4. The effect of glycerol/water ratio on the rheological properties of waxy starch melt. Total plasticiser content = 70%.

3.3. Effect of glycerol/water ratio

Fig. 4 shows the effect of glycerol/water ratio on the rheological properties of TPS. The total plasticiser content was fixed at 70%. Again, a strong power-law dependence of viscosity on shear rate can be observed. It can be seen that the higher the glycerol/water ratio, the higher the viscosity. In addition, the sample at higher glycerol/water ratio showed a stronger shear-thinning behaviour. Moreover, for samples at 1:4 and 2:3 glycerol/water ratios, higher temperature could also strengthen the shear-thinning behaviour.

3.4. Rheological model of thermoplastic starch

Based on the results observed in Figs. 3 and 4, a power-law model can be used to describe the relationship between viscosity and shear rate (Della Valle et al., 1996; Martin et al., 2003; Xie et al., 2009):

$$\eta = K\dot{\gamma}^{n-1} \tag{4}$$

where η is the viscosity (Pa s) of TPS, $\dot{\gamma}$ the shear rate (s), K the consistency (Pa s), and n the power-law index. For a pseudoplastic material, $n < 1$; the more the n value approaches 1, the more Newtonian behaviour the material shows.

Table 2 lists the detailed parameters of regressed power-law model for different samples at different conditions. No obvious trend was observed for the change of the power-law index n with the total plasticiser content. Similar result has been observed for wheat starch plasticised by glycerol and water (Rodriguez-Gonzalez, Ramsay, & Favis, 2004). Also, Willett et al. (1997) reported that the effect of water (as sole plasticiser) on n was not clear for waxy maize starch. In contrast, there was an evident trend for n to increase with decreasing glycerol/water ratio, indicating the greater tendency of water to influence the TPS in a Newtonian way than glycerol. This may be because the small molecules of water can be more effective to facilitate the formation of gell-balls (comprised mainly of chains from the same sub-main chain, like opened umbrella) and super-globes (formed by one amylopectin molecule) of waxy maize starch and lubricate these gell-balls and super-globes (Xie et al., 2009; Yu & Christie, 2005), so there was less viscosity change with the variation of shear rate when water dominated as the plasticiser. Moreover, for samples at lower glycerol/water ratios (1:4 and 2:3), n was apparently higher at higher temperature. It is probable that the formation and lubrication of gell-ball and super-globes in the presence of water are more effective at higher temperature.

Table 2 also shows the power-law consistency K increased with decreasing temperature, decreasing total plasticiser content, and increasing glycerol/water ratio. This is in agreement with previous studies (Martin et al., 2003; Rodriguez-Gonzalez, Ramsay, & Favis, 2004; Willett et al., 1997; Xie et al., 2009). Since K has a direct relationship with viscosity (see Eq. (4)), it can be used to represent the viscosity characteristics of a material under certain conditions. The K results are as expected, since both temperature and plasticiser have a negative effect on the viscosity, and the plasticiser of lower molecular weight has a greater effect on lowering the viscosity.

Table 2
Power-law parameters of starch melt at different conditions.

Total plasticiser content (%)	Glycerol/water ratio	Temperature (°C)	Consistency K (Pa s^n)	Power-law index n	Correlation coefficient (R^2)
70	1:4	90	965.79	0.6497	0.9851
70	1:4	110	155.46	0.8101	0.9425
70	1:4	130	30.52	0.9278	0.6257
70	2:3	90	10363.82	0.3081	0.9412
70	2:3	110	1766.65	0.5582	0.9556
70	2:3	130	838.66	0.6435	0.9626
70	3:2	90	14540.65	0.5076	0.9883
70	3:2	110	3866.04	0.6039	0.9914
70	3:2	130	3543.58	0.4941	0.9933
90	3:2	90	850.29	0.5764	0.9854
90	3:2	110	496.33	0.5391	0.9668
90	3:2	130	179.06	0.6280	0.9966
110	3:2	90	281.48	0.6097	0.9844
110	3:2	110	111.08	0.6607	0.9824
110	3:2	130	91.15	0.6210	0.9898

To better understand the effect of plasticiser on the rheological properties of TPS, the previous models in terms of power-law parameters have been used with modification. The power-law index n can be expressed as (Della Valle et al., 1996):

$$n = n_0 + \alpha_1 T + \alpha_2 \mathrm{GC} + \alpha_3 \mathrm{MC} + \alpha_{12} T \cdot \mathrm{GC} + \alpha_{13} T \cdot \mathrm{MC} + \alpha_{23} \mathrm{GC} \cdot \mathrm{MC} + \alpha_{123} T \cdot \mathrm{GC} \cdot \mathrm{MC} \qquad (5)$$

where T is the absolute temperature (Kelvin) of TPS, GC the glycerol content (w/w, dry basis), MC the moisture content (w/w, dry basis), and n_0, α_1, α_2, α_3, α_{12}, α_{13}, α_{23} and α_{123} the constants. By linear regression, the constants are calculated: $n_0 = 13.03$, $\alpha_1 = 0.03180$, $\alpha_2 = 37.76$, $\alpha_3 = 20.09$, $\alpha_{12} = 0.09083$, $\alpha_{13} = 0.04444$, $\alpha_{23} = 70.84$, and $\alpha_{123} = 0.1683$. The correlation coefficient is 0.8861, which is satisfactory.

The consistency K can be expressed as (Martin et al., 2003):

$$K = K_0 \exp\left[\frac{E}{R}\left(\frac{1}{T}\right) - \alpha \mathrm{GC} - \alpha' \mathrm{MC}\right] \qquad (6)$$

where E/R is the reduced flow activation energy (Kelvin) and K_0 another constant (Pa s^n). By linear regression, the constants are calculated: $K_0 = 0.03073$, $E/R = 7396$, $\alpha = 5.564$, and $\alpha' = 17.15$. The correlation coefficient is 0.8729, which is also satisfactory. The constants found here are in very good agreement with the values from previous studies (Aichholzer & Fritz, 1998; Della Valle et al., 1995; Martin et al., 2003; Willett et al., 1995).

From these calculated constants, it is clear that glycerol had a greater influence on both n and K than water. Regarding n, the combination of glycerol and water had even a larger influence. However, the impact of temperature on n was quite small.

3.5. Mastercurve study

In order to emphasise the differences among rheological behaviours of different TPS samples under different conditions, a master curve can be drawn using the classical time–temperature superposition, extended to include moisture and glycerol contents (Della Valle et al., 1996; Vergnes, Della Valle, & Tayeb, 1993). This makes it possible to gather all of experimental data in this work for comparison purpose. The reduced viscosity, η/a_{TGCMC}, can be plotted against the reduced shear rate, $\dot{\gamma}\, a_{\mathrm{TGCMC}}$, where a_{TGCMC} is the shift factor defined as:

$$a_{\mathrm{TGCMC}} = \exp\left[\frac{E}{R}\left(\frac{1}{T_i} - \frac{1}{T_0}\right) - \alpha(\mathrm{GC}_i - \mathrm{GC}_0) - \alpha'(\mathrm{MC}_i - \mathrm{MC}_0)\right] \qquad (7)$$

where the subscript i indicates the flow conditions to be superposed on the reference flow conditions, which is labelled by the subscript 0. Here, the reference conditions are: $T_0 = 110\,^\circ\mathrm{C}$, $\mathrm{GC}_0 = 54\%$, and $\mathrm{MC}_0 = 36\%$. Thus, the mastercurve is drawn in Fig. 5. It is interesting to note in Fig. 5 that the rheological behaviours of waxy starch melt can be divided into three groups: (1) When glycerol/water ratio was 3:2, the samples with 90% and 110% total plasticiser content showed similar rheological behaviour; (2) when the total plasticiser content reduced to 70% (the glycerol/water ratio kept at 3:2 or even further decreased to 2:3), the viscosity was shifted to higher value, but with quite similar shear-thinning behaviour (similar slope); (3) when the glycerol/water ratio was reduced to 1:4 (but the total plasticiser content was kept at 70%), the sample showed less shear-thinning behaviour.

Since the starch samples were allowed to finish their fully transformation before rheological measurements, and the time–temperature–moisture content–glycerol content superposition has been applied, the differences shown on the mastercurve can only be related to interaction between starch and plasticiser (water and glycerol) molecules and their structural impact. Fig. 6 shows the schematic representation of microstructural changes of starch under processing with different plasticisers. As discussed before, the small molecules of water can be more effective to facilitate the formation of gell-balls and super-globes of waxy maize starch molecules and lubricate them. Thus, the movements of such "balls" require much less energy compared to that of amylopectin molecules in other states. As a result, TPS showed a more Newtonian behaviour when the glycerol/water ratio was low. However, when the glycerol/water ratio was higher, the chains from the same sub-main chain of amylopectin molecule were not unfolded so much due to the formation of stronger hydrogen bonds between amylopectin branches and molecules by glycerol molecules. In this case, the "ball" effect was weak and the waxy TPS behaved more like a normal polymer and showed stronger shear-thinning behaviour. When the plasticiser content increased to be higher than a specific level (90% and 110%), the rheology actually reflected the behaviour of the blends of plasticiser (glycerol/water ratio) and starch, which was thus shown as another case observed on the mastercurve.

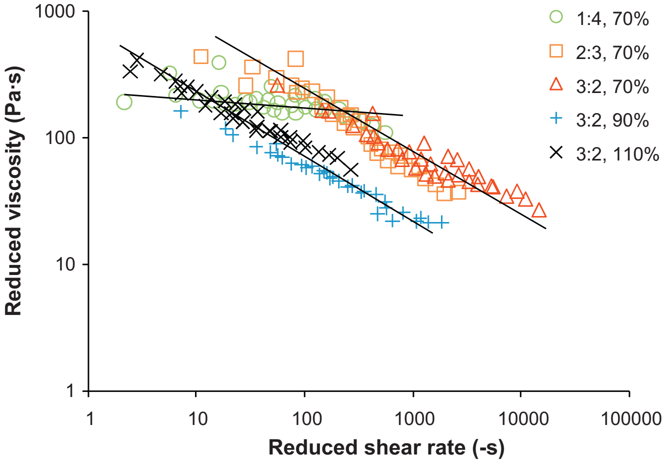

Fig. 5. Matercurve of rheological results of waxy starch melt at $T_0 = 110\,^\circ\mathrm{C}$, $\mathrm{GC}_0 = 54\%$, and $\mathrm{MC}_0 = 36\%$, obtained by time–temperature–moisture content–glycerol content superposition.

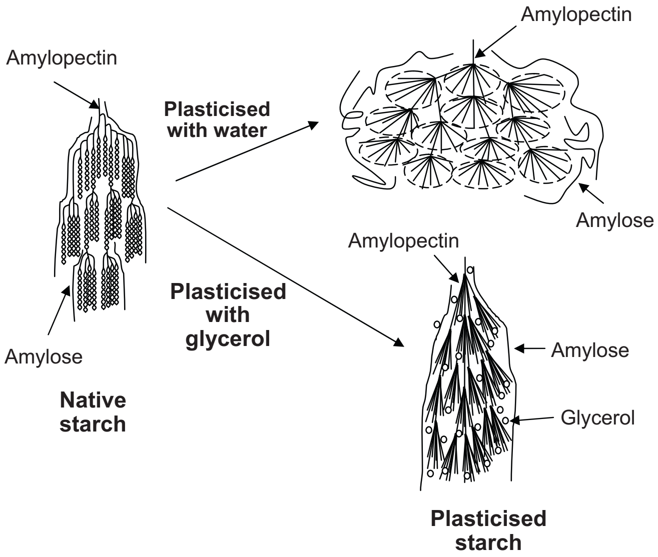

Fig. 6. Schematic representation of microstructural changes of starch under processing with different plasticisers.

4. Conclusion

This study involved using the MPR to study the rheological properties of TPS melt. This facility has the advantages of requiring a small amount of sample, preventing the loss of moisture, and pressurising the sample; thus it is suitable to characterise the melt rheology of TPS. Since the samples were well transformed into TPS with a stable molecular and rheological state before any meaningful rheological measurements, it was possible to investigate the effects of temperature, total plasticiser content, and glycerol/water ratio in an accurate way.

The TPS showed a shear-thinning behaviour, with the viscosity decreased with increased shear rate. Power-law model ($\eta = K\dot{\gamma}^{n-1}$) was proved to be appropriate in describing the relationship between viscosity and shear rate. For the power-law index *n*, the combination of glycerol and water had the greatest influence, followed by glycerol alone and water, while temperature had little impact. For the consistency *K*, glycerol also had greater influence than water. By plotting the mastercurve of the results tested at different conditions, it is interesting to note that the sample showed less shear-thinning behaviour at 1:4 glycerol/water ratio than the samples at higher glycerol/water ratio; however, the total plasticiser content showed little effect on the shear-thinning behaviour.

During plasticisation of native starch with mainly water, the amylopectin molecules can form “ball” like shapes by greatly unfolding their branches. These “balls” are easy to move, so more Newtonian like behaviour is shown. However, when the starch is plasticised mainly by glycerol, the “balls” are largely absent, and the amylopectin molecules behave more like a normal polymer and shows stronger shear-thinning behaviour. Further study will be carried out to investigate other plasticisers and their combination on the rheological properties of TPS.

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