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Rheological properties of thermoplastic starch studied by multipass rheometer

Suzlin Tajuddin[a], Fengwei Xie[b,*], Timothy M. Nicholson[a,**], Peng Liu[c], Peter J. Halley[a,b]

[a] Centre for High Performance Polymers, School of Chemical Engineering, The University of Queensland, St Lucia, Qld 4072, Australia
[b] Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, St Lucia, Qld 4072, Australia
[c] ERCSPP, College of Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, China

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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

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

* Corresponding author. Tel.: +61 7 3346 3199; fax: +61 7 3346 3973.
** Corresponding author. Tel.: +61 7 3365 4081; fax: +61 7 3365 4199.
E-mail addresses: f.xie@uq.edu.au, fwhsieh@gmail.com (F. Xie), t.m.nicholson@uq.edu.au (T.M. Nicholson).

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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.

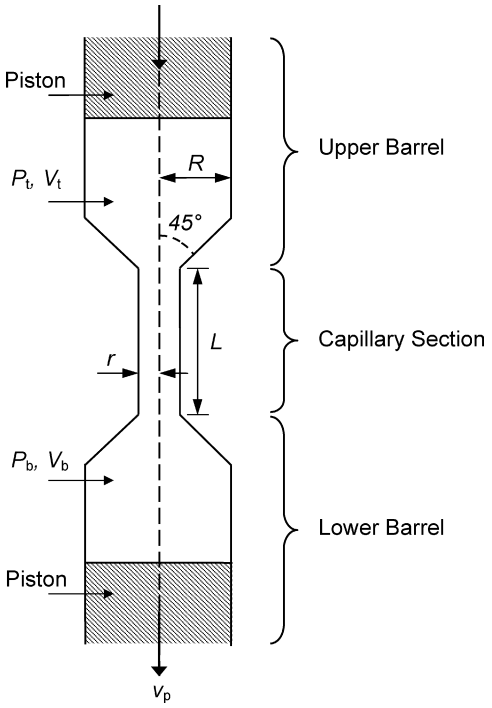

Fig. 1. Schematically representation of multipass rheometer. The barrel/piston radius (R) was 5 mm; the capillary radius (r) used was 2 mm; the capillary lengths (L) used were 1 mm, 10 mm, and 40 mm; P_t and P_b represent the pressure in the top and bottom barrel, respectively; V_t and V_b represent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