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Rheology to understand and optimise processibility, structures and properties of starch polymeric materials

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1 **ABSTRACT**

2 This paper reviews the state of the art in the field of the rheology of starch
3 polymers, including specially designed rheometric techniques and complex rheology
4 as influenced by different conditions. In terms of rheometric techniques, off-line
5 extruder-type capillary/slit rheometers are commonly used but subsequent changes
6 during measurement often occur as starch structures are highly sensitive to
7 thermomechanical treatment. An in-line rheometer set-up with a double-channel die
8 incorporated to the processing extruder is a direct and effective method to minimise
9 the processing history change at different testing shear rates. In addition, pre-shearing,
10 multipass, and mixer-type rheometers are also suitable for starch polymers. The
11 rheological behaviour of starch polymeric materials can be greatly impacted by their
12 formulation (botanical source, plasticiser and additive type and content, and the
13 structure related to blend or composite) and processing conditions (temperature,
14 mechanical energy, etc). Starch polymer melts exhibit shear-thinning and extension-
15 thinning behaviours, and shows strong elastic properties. A wide range of rheological
16 models, considering formulation and processing conditions, have been reviewed for
17 different multiphase systems. The rheological behaviour can also be related to the
18 compatibility (blends, composites), expansion/foaming properties, film blowing
19 properties, etc.. The significance of processing rheology of starch polymers lies in
20 characterising the complex melting and flow behaviours, characterising the
21 viscoelastic properties, determining optimal processing method and conditions, and
22 better controlling the quality of the final products.

23

24 *Keywords:*

25 Starch; Melt; Processing; Rheology; Rheometry; Shear; Extension

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Nomenclature

CDV, capillary/cylindrical die viscometer

DCD, double-channel die

DP, degree of polymerisation

DSC, differential scanning calorimetry

EPMA, propylene maleic anhydride

GMS, glycerol monostearate

LDPE, low density polyethylene

LLDPE, low linear density polyethylene

MDI, methylenedipheny diisocyanate

MPR, multipass rheometer

PBSA, poly(butylene succinate adipate)

PCL, polycaprolactone

PE, polyethylene

PHEE, poly(hydroxy ester ether)

PLA, polylactide

POES, polyoxyethylene stearate

PVA, polyvinylalcohol

REX, reactive extrusion

sc-CO₂, supercritical carbon dioxide

SDV, slit die viscometer

SEI, cross-sectional expansion index

SEM, scanning electron microscopy

SME, specific mechanical energy

SSE, single-screw extruder

TEG, triethylene glycol

TPS, thermoplastic starch

TSE, twin-screw extruder

VEI, volumetric expansion index

WLF, Williams-Landel-Ferry

XRD, X-ray diffraction

a , the Carreau-Yasuda fitting parameter

C_s , starch concentration

dP/dL , pressure gradient along the die channel

E/R , reduced flow activation energy

GC , glycerol content

GC_0 , reference glycerol content

K , consistency coefficient in shear viscosity model

L , length of a capillary

MC , moisture content

MC_0 , reference moisture content

n , power-law index in shear viscosity model

N , screw/rotor speed

N_1 , first normal stress difference

N_c , cell number density of a foam

P_a , ambient pressure

P_b , vapour pressure inside a bubble of a foam

Q , volumetric flow rate or feed rate

q_v , viscous heat dissipation in power per unit volume

R , foam bubble radius

r , radius of a capillary

\dot{R} , the rate of change in R

S , consistency coefficient in extensional viscous model

t , power-law index in extensional viscous model

T , temperature

T_0 , reference temperature

T_g , glass transition temperature

T_r , Trouton ratio

x , degree of starch transformation

$\dot{\gamma}$ shear rate

Γ , torque

$\dot{\epsilon}$, extensional rate

η_{T_g} , shear viscosity at glass transition temperature

η_0 , shear viscosity at zero shear rate

η_{add} , theoretical shear viscosity calculated by the log-additive mixing rule

η_e , extensional viscosity

η_{exp} , experimented shear viscosity

η_p , planar extensional viscosity

η_s , shear viscosity

η_u , uniaxial extensional viscosity

λ , is the relaxation time

σ , surface tension (foam)

τ_0 , yield stress in Herschel-Bulkley model

τ_{11} , normal stress along the direction of flow

τ_{22} , normal stress along the velocity gradient

ϕ , strain history,

Φ , volumetric fraction

ψ , time-temperature history

1 **1. Introduction**

2 Due to the environmental concerns and the shortage of oil, the use of starch
3 resources in non-food applications has experienced considerable development in the
4 past decades in order to find substitutes to petroleum-based plastics. Starch has
5 advantages such as low cost, wide availability, and total compostability without toxic
6 residues, though there are also issues on the availability of agricultural surfaces to
7 make plants at world scale. By using conventional processing techniques such as
8 extrusion, native granular starch (also known as raw starch) can be converted into a
9 molten state with the presence of low content of plasticisers such as water and
10 glycerol. Since the first studies have shown that the starch polymer melt behaves, in
11 part, like a standard synthetic polymer, this material is often referred as
12 “thermoplastic starch (TPS)” in literature. TPS can be processed into various
13 products such as sheets/films, foams, and other specific shapes by extrusion, injection
14 moulding, compression moulding, and other processes [1]. The processing conditions
15 are dependent on the techniques used and/or the final products. For example, starch-
16 polyester blends are processed in melt state under high shear, 10^2 – 10^3 s⁻¹ in extrusion
17 and 10^3 – 10^4 s⁻¹ in injection moulding [2]. The knowledge of the rheological
18 behaviour of starch polymer melts during processing is a key point in 1)
19 understanding the melt microstructure as affected by the processing conditions, 2)
20 solving fundamental flow-related engineering problems, 3) determining optimal
21 processing conditions, and 4) better controlling the quality of the final products. The
22 critical role of rheology in starch polymer processing is illustrated in [Fig. 1](#).

23

24 [Insert [Fig. 1](#) here]

25

1 The rheology of starch polymers, however, is not a simple issue. While water acts
2 as a destructuring agent and an efficient but volatile plasticiser during processing,
3 most rheometers cannot preserve the water content, which makes the rheological
4 measurements often impossible. Secondly, the massive macromolecular changes
5 under thermomechanical treatment during rheological measurement result in
6 subsequent changes in rheological properties which are difficult to follow. This is in
7 contrast to a standard synthetic polymer like polyethylene (PE), which is relatively
8 stable during processing and measurement. Thirdly, the viscosity of starch polymer
9 melt is much higher than that of most synthetic polymers, which also makes the
10 rheological characterisation difficult. The frequent use of different plasticisers and
11 additives for the purpose of reducing the viscosity and improving the processibility
12 further make the rheological properties of starch polymer melts difficult to understand.
13 In all, these difficulties have led to incorrect or missing information on processing
14 rheology of starch polymers, and this itself can be one of the biggest hurdles in the
15 development of new environmentally friendly starch polymeric materials.

16 Although starch polymers and their processing have already been well reviewed in
17 several papers [1,3-10], the rheological behaviour and the analysis of the rheology-
18 processing relationships has not been a focus. This review reports on the state of the
19 art in the field of the rheology of starch polymers including the specially designed
20 rheometric techniques and the complex rheological behaviours as influenced by
21 different conditions. The backgrounds of starch fundamentals and processing are also
22 given. It is believed that a clear understanding of the rheological properties of starch
23 polymer melts is crucial in the processing for the next generations of low-moisture
24 starch-based foods and bioplastic materials.

25

1 **2. Starch fundamentals**

2 *2.1. Structures of starch*

3 The starch granule provides the main way of storing energy over long periods in
4 green plants [11]. Starch granules are mainly found in seeds, roots, and tubers, and
5 are from origins such as maize (corn), wheat, potato, and rice. Native starch granules
6 are well known to have multilevel structures from macro to molecular scales, i.e.
7 starch granules ($<1\ \mu\text{m}\sim 100\ \mu\text{m}$), alternating amorphous and semicrystalline shells
8 (growth rings) ($100\sim 400\ \text{nm}$), crystalline and amorphous lamellae (periodicity)
9 ($9\sim 10\ \text{nm}$), and macromolecular chains ($\sim\text{nm}$) [11-14]. Native starch granules present
10 a concentric 3D architecture from the hilum with a total crystallinity varying from
11 15% to 45% depending on the particular plant species [15]. Starch is a polysaccharide
12 consisting of D-glucose units, referred to as homoglucon or glucopyranose. The two
13 major biomacromolecules of starch are amylose and amylopectin. Amylose is a
14 sparsely branched carbohydrate mainly based on $\alpha(1-4)$ bonds with a molecular
15 weight of 10^5-10^6 and can have a degree of polymerisation (DP) as high as 600 [11].
16 The number of macromolecular configurations based on $\alpha(1-6)$ links is directly
17 proportional to the amylose molecular weight [16]. The chains show spiral-shaped
18 single- or double-helices with a rotation on the $\alpha(1-4)$ link and with six glucoses per
19 rotation, where the hydroxyl groups are mainly located toward the exterior of the
20 helices. On the other hand, amylopectin is a highly multiple-branched polymer with a
21 high molecular weight of 10^7-10^9 . It is one of the largest natural polymers known
22 [11]. Amylopectin is based on $\alpha(1-4)$ (around 95%) and $\alpha(1-6)$ (around 5%) links,
23 with constituting branching points localised every 22-70 glucose units, generating a
24 kind of grape-branch-like structure with pending chains of $\text{DP} \approx 15$. This specific
25 structure has a profound effect on the physical and biological properties [11,13].

1 Besides, in starch granules are also found very small amounts of proteins, lipids and
2 phosphorus depending on the botanical resource [12,13]. These components can
3 interact with the carbohydrate chains during processing (e.g. Maillard reaction) and
4 then modify the behaviour of the starchy materials. The highly hydrophilic nature of
5 starch is by the cause of the abundance of hydroxyl groups in the polysaccharides by
6 genetic selection.

7 Depending on the source, amylose content of starch can be varied from <1% to
8 70%. The so-termed waxy starch contains little or no amylose, whereas high-amylose
9 starch contains >50% amylose. [Tab. 1](#) gives an overview of the structural properties
10 of maize starches with different amylose contents [17]. Starches with different
11 amylose contents have quite different thermal, rheological, and processing properties.

12

13 [Insert [Tab. 1](#) here]

14

15 2.2. *Gelatinisation/melting of starch*

16 When native starch granules are heated in water, their semicrystalline nature and
17 3D architecture are gradually disrupted, resulting in the phase transition from an
18 ordered granular structure into a disordered state in water, which is known as
19 “gelatinisation” [18-20]. Gelatinisation is an irreversible process that includes, in a
20 broad sense and in time/temperature sequence, granular swelling, native crystalline
21 melting (loss of birefringence) and molecular solubilisation [21]. Full gelatinisation
22 of starch under shearless conditions requires excess water, which Wang et al. [22]
23 have defined as >63% for waxy maize starch for example. If the water concentration
24 is too high, the crystallites in starch might be pulled apart by swelling, leaving none to
25 be melted at higher temperatures. If the water concentration is limited, the swelling

1 forces will be much less significant and the steric hindrance is high. Thus, complete
2 gelatinisation will not occur in the usual temperature range [23-25]. However, as the
3 temperature increases, starch molecules will become progressively more mobile and
4 eventually the crystalline regions will be destructured [26]. The process of
5 gelatinisation with a low water content could more accurately be defined as the
6 “melting” of starch [24].

7 The gelatinisation/melting behaviour of starch is quite different when shear
8 treatment is imposed [27]. It has been shown that shear can enhance the
9 destructurement of starch granules in abundant water [28,29] and the melting of
10 crystallites with limited water [30-32]. The significance of such studies is that most
11 processing techniques for starch polymers involve shear treatment. In extrusion
12 processing, shear forces can physically tear apart the starch granules, allowing faster
13 transfer of water into the interior molecules [33]. Therefore, during extrusion, the loss
14 of crystallinity is not only caused by water penetration, but by the mechanical
15 disruption of molecular bonds due to the intense shear fields within the extruder [34-
16 37].

17

18 **3. Starch processing**

19 *3.1. Processing strategies*

20 The techniques that have been used to process starch polymers, such as internal
21 mixer, extrusion, injection moulding, compression moulding, and film casting, are
22 similar to those widely used for standard synthetic thermoplastics. Among these
23 techniques, extrusion is the most widely used. A single-screw extruder (SSE) can
24 handle the high viscosity of starch and provide a high processing pressure for
25 continuous metering of starch through die shapes. A twin-screw extruder (TSE) has a

1 large operational flexibility (individual barrel zone temperature control, multiple
2 feeding/injection, and screw configuration for different degree of mixing/kneading)
3 and is useful for intensive mixing and compounding of components into starch
4 plastics. Another advantage of TSE is to allow the decoupling of die flow and
5 mechanical treatment. In both SSE and TSE, residence times and specific mechanical
6 energy (SME) inputs can be controlled, and high efficiency production can be
7 achieved. Other processing techniques such as film blowing and injection moulding
8 are often combined with extrusion. More details about the specifics of processing
9 techniques for starch polymers can be found in another review paper [1].

10 Starch cannot be thermally processed without water. By reducing the moisture
11 content, the melting temperature of starch would progressively increase, and that of
12 dry starch is often larger than its decomposition temperature as extrapolated by Flory
13 Law [38,39]. Water functions by lowering the melting temperature and plasticising
14 the starch polymer. As a result, in practical processing, water acts as a “plasticiser”.
15 However, unstable processing may be caused due to the evaporation of water. Further,
16 the final products based on starch containing only water usually have poor mechanical
17 properties especially due to the brittleness since its final temperature is lower than its
18 glass transition temperature (T_g). To overcome these issues, non-volatile (at the
19 processing temperature) plasticisers such as polyols (glycerol, glycol, sorbitol, etc.)
20 [40-43] and compounds containing nitrogen (urea, ammonium derived, amines)
21 [43,44] are utilised. Also, citric acid [40] has been used as non-volatile plasticisers to
22 prepare TPS.

23 Various lubricants have been used to improve the processibility of starch
24 polymeric materials, such as magnesium stearate [45], calcium stearate [46], and

1 fluoro-elastomers [43]. The use of a lubricant during processing can reduce the
2 tendency of the material to stick to the die and clogging it.

3 To improve the product performances such as moisture resistibility, mechanical
4 properties, and long-term stability, starch is often blended with other (especially
5 biodegradable) polymers such as polylactide (PLA) [2,47-52], polycaprolactone (PCL)
6 [2,47,53,54], poly(butylene succinate adipate) (PBSA) [2,54], poly(hydroxy ester
7 ether) (PHEE) [55], and polyvinyl alcohol (PVA) [56,57].

8

9 *3.2. Issues related to processing*

10 The processing of starch, however, is much more complex and difficult to control
11 than for many other polymers. Fig. 2 gives a schematic representation of starch
12 processing by extrusion. While the processing of most synthetic polymers constitutes
13 melting, blending/compounding, and shaping, the processing of starch also involves
14 the transformation (granular disruption, crystalline melting, etc.) of starch from a
15 native granular state to a molten state. To produce a homogeneous molten state, high
16 energy input (high SME, $>10^2$ kWh/t) is needed [58-60]. However, sometimes we
17 can observe residual granules in starch polymer melt [31,32,61], which means the
18 starch granular transformation is not 100%. In addition, Starch macromolecular
19 degradation under processing especially with the shear treatment has been studied
20 [24,62,63]. The level of degradation depends on the processing conditions and
21 formulation such as plasticiser type and content, temperature, and total SME
22 [62,64,65]. In addition, the processing can affect amylopectin much more than
23 amylose due to the large size, the highly branched structure, and the inflexible chains
24 of the former [66,67]. Both granular transformation and macromolecular degradation

1 which are influenced by the processing, can, in turn, impact the processibility
2 (rheology) and product properties.

3

4 [Insert Fig. 2 here]

5

6 **4. Rheometry for starch polymers**

7 Since high energy input ($SME > 10^2$ kWh/t) is needed to obtain a homogeneous
8 molten state for rheological measurement, the number of rheometers used in the
9 studies of starch polymer melts is limited. Tab. 2 gives a comparison of these
10 rheometers and more details are as followed.

11

12 [Insert Tab. 2 here]

13

14 *4.1. Backgrounds*

15 Details in polymer rheology and rheometry can be found in a number of books
16 [68-71].

17 Regarding the rheology of starch polymer melts, most literature has dealt with
18 steady shear viscosity (η_s), which can be measured by forcing a polymer melt through
19 a capillary/cylindrical die viscometer (CDV) or slit die viscometer (SDV) and
20 calculated based on the melt flow rate and the pressure drop across the die channel. A
21 SDV is preferably used since pressure transducers can be more easily flush-mounted
22 along the channel and thus pressure gradient (dP/dL) along the channel can be
23 obtained. In this case, the obtained result is more accurate than that from a CDV
24 where only inlet pressure is usually measured and the excess pressure drop is
25 accounted for by Bagley correction [72,73].

1 Comparing with shear viscosity, extensional viscosity (η_e) has been much less
2 focused for starch polymers. It can be obtained from entrance pressure drop
3 measurement made on a CDV or SDV [74-76]. The entrance pressure can be
4 determined either from Bagley plots when a CDV is used, or by subtracting the
5 extruder barrel head pressure with the extrapolated pressure at the entrance of the die
6 when a SDV is used. Different analysis methods in extensional flow have been
7 compared for starch polymer melts [77,78]. It has been suggested that extensional
8 viscosity can be used to evaluate the elastic properties of polymer melts [71,74].

9 Another way to evaluate the elasticity is to use first normal stress difference (N_1),
10 which has also not been widely reported for starch polymer melts. It is defined as:

11
$$N_1 = \tau_{11} - \tau_{22} \tag{1}$$

12 where τ_{11} is the normal stress along the direction of flow, and τ_{22} is the normal stress
13 along the direction of the velocity gradient. An SDV can easily be adapted for the
14 measurement of N_1 by exit pressure method [79] or hole pressure method [80-82]. In
15 the first method, since exit pressure is obtained by extrapolating the pressure
16 measurements along the die to the exit, both positive and negative values have been
17 obtained for starch polymer melts [77,83,84]. The erratic results can be ascribed to
18 such reasons as the under-developed flow or water evaporation-induced foaming at
19 the exit. It has been shown that the hole pressure method is more reliable than the exit
20 pressure method for starch polymer melts [85].

21

22 *4.2. “Off-line” rheometry*

23 As previously stated (Section 3), the most efficient way to process starch is by
24 single-/twin-screw extrusion. After extrusion processing, the rheological properties of
25 TPS can be tested at desired conditions in a separate facility. This is defined here as

1 “off-line” rheometry, understood as “off the initial extrusion processing line”. In
2 terms of the measurement principles, the category includes rotational rheometer,
3 plunger-type capillary/slit rheometer, and extruder-type capillary/slit rheometer.
4

5 *4.2.1. Rotational rheometer*

6 A rotational rheometer is a particular type of rheometer in which shear is produced
7 by a drag flow between a moving part and a fixed one, which forms such geometries
8 as plate-plate, cone-plate, and concentric cylinders [69]. The tested material is located
9 between the two parts and is exposed to the environment. Though this type of
10 rheometer has regularly been utilised to study the rheological properties of starch gels
11 or pastes (with high water content, > 95%) [86,87], it is quite difficult to use it for the
12 rheological measurements of starch polymer melts due to too low SME input, and
13 water evaporation at high temperature. In addition, the high viscosity of starch
14 polymer melts usually surpasses the torque capacity of such a rheometer. Della Valle
15 and Buleon [88] used a plate-plate geometry and coated the sample outer edge with
16 silicon grease to reduce the evaporation of water; however, the water evaporation was
17 still obvious as shown in time sweep test. Despite of the difficulty, this rheometer
18 remains to be an interesting tool, in some precise conditions, to study the properties of
19 some starchy materials.
20

21 *4.2.2. Plunger-type capillary/slit rheometer*

22 A plunger-type capillary/slit rheometer consists of a barrel where the material is
23 loaded, a plunger (also piston) for compressing and pushing the material, and a
24 capillary/slit die which is attached at the end of the barrel. After the material is loaded
25 into the barrel and melted at a desired temperature, the plunger can move towards the

1 die at a series of pre-selected speeds. The material is thus forced through the die
2 channel. The flow rate can be calculated with the plunger speed along with its
3 geometry data. The total pressure drop through the barrel and capillary can be
4 calculated with either the load on the plunger or a pressure transducer mounted on the
5 barrel. Alternatively in some latest designs (e.g. Instron[®] CEAST SmartRheo Series),
6 the dP/dL can be calculated by a series of pressure transducers flush-mounted through
7 a slit die channel. Consequently, shear rate and shear stress, and thus viscosity, can be
8 calculated. Particularly, some recent developed rheometers (e.g. Malvern[®] Rosand)
9 have twin-bore units which allows simultaneous measurements on both long and short
10 dies to determine the inlet pressure drop at the die, and therefore the absolute viscosity
11 by Bagley method. On the other hand, when some specially designed dies such as
12 zero-length die were used, the kind of rheometers can be employed to estimate the
13 extensional flow characteristics of polymer samples.

14 One of the greatest advantages of a plunger-type capillary/slit rheometer is their
15 wide range of shear rate, roughly between 2.5×10^{-1} and $5 \times 10^4 \text{ s}^{-1}$ according to the
16 literature [2,44,47,49-51]. Besides, the rheometer is easy to use and requires
17 relatively small amount of sample to be tested. Moreover, the material is subjected to
18 much less shear treatment when a plunger-type capillary/slit rheometer is used
19 compared to an extruder-type capillary/slit rheometer (discussed in the following
20 section) [89]. As a result, this rheometer has been widely used for the rheological
21 measurements of TPS prepared by extrusion processing [2,40,43-45,47,49-
22 51,56,57,83,89-96].

23 In some studies [97-99], this rheometer has been directly used as a processing tool,
24 in which native granular starch pre-blended with plasticiser is only applied with high
25 temperature and high pressure. The problems with this method are the SME is rather

1 low or even absent, and that heat diffusion is not uniform. Thus, a homogeneous
2 molten state of starch can hardly be achieved like in extrusion processing.

3 A pre-shearing rheometer called “Rheoplast[®]” has been designed for the
4 rheological studies of starch polymer melts [100-103]. The schematic representation
5 of this rheometer is shown in Fig. 3. It combines the features of a Couette rotational
6 system, in which a mechanical treatment may be applied and the melting is executed,
7 and of a capillary rheometer in which the viscosity is measured. The main advantages
8 of the Rheoplast include [100,101]:

- 9 • The material is subjected to a well characterised thermomechanical treatment
10 (under specific shear rate, melt temperature, and shearing time): The shear rate is
11 determined by the rotation rate of the inner piston; the melt temperature is
12 controlled by the circulation of a thermostated fluid through channels around the
13 barrel, and the shearing time is the time for which the inner piston is rotated.
- 14 • The different parameters of treatment (shear rate, melt temperature, and shearing
15 time) are independent, unlike those of an extruder in which, for example,
16 increasing screw speed leads to the modification of residence time.

17

18 [Insert Fig. 3 here]

19

20 Vergnes et al. [101] claimed that Rheoplast can be as a useful tool for the
21 simulation of the processing in an extruder because the treatment intensity in the
22 Rheoplast (rotation speed: 200–700 rpm; melt temperature: 140–180°C; shearing time:
23 5–40 s) are of the same order of magnitude as those encountered in extrusion
24 processing. However, Martin et al. [84] found that the viscosity measured by in-line

1 viscometer is lower than that by Rheoplast due to the difference of SME leading to
2 different macromolecular degradation.

3 In operation, there are also some problems associated with the Rheoplast such as
4 the loss of moisture at high temperature and the tampering of measurement by the
5 remaining product in the convergent entry and the capillary itself [100]. To overcome
6 these issues, a number of repetitions are important for each value of the pushing-down
7 velocity of the inner piston (i.e. for each value of the flow rate through the capillary)
8 [100]. Bagley corrections are also critical and can be applied by using capillaries with
9 different length to radius (L/r) ratios [100,102,103].

10 The Rheoplast can also be used as an off-line rheometer to test the rheological
11 properties of TPS prepared by other methods such as extrusion [103]. Moreover, it is
12 interesting to read in some literature [34,104] that this facility has also been used
13 solely as a processing tool without capillary.

14

15 4.2.3. *Extruder-type capillary/slit rheometer*

16 The extruder-type capillary/slit rheometer is actually a CDV or SDV incorporated
17 to an extruder which functions for remelting and feeding the material into the
18 viscometer. The extruder used here is mostly a SSE (choke-fed extruder) with a
19 compression screw [11,52,54,65,105-107]. The rotation of the screw forces the
20 material through the die rheometer and the shear rate can be varied with the screw
21 rotation speed. In this technique, either the Bagley method (for CDV) [65,95,108] or
22 the pressure gradient method (for CDV or SDV) [52,54,107,108] has been used to
23 measure the viscosity of starch polymer melts.

24 Due to the set-up, this technique usually requires a relatively large amount of
25 sample for a test compared to a plunger-type capillary/slit rheometer. However, it can

1 work more efficiently because the extrusion is carried out in a continuous way without
2 waiting time for sample melting. Besides, this technique is suitable when multiple
3 extrusion runs are required especially for TPS blends and composites [52,54].
4 Furthermore, this technique also allows some post-extrusion processes such moisture
5 content conditioning to be carried out before the rheological measurements [65,108].

6 The use of a separate extrusion run for rheological measurement, however, may
7 increase the macromolecular degradation especially with starch which is highly
8 sensitive to the thermomechanical history [65]. Therefore, the measured viscosity of
9 TPS by this method was usually lower than by an in-line extrusion rheometer
10 (discussed in [Section 4.3](#)) [43,84]. Besides, the change in screw speed for different
11 shear rates also changes the processing history, which results in different product to
12 be tested at different shear rate. However, in some particular studies, the shear rate
13 was controlled by a speed-controlled piston in the die [106] or a side-stream valve at
14 the end of the extruder barrel [105], which greatly reduced the thermomechanical
15 history difference. Since the latter method has mostly been used in an in-line
16 rheometry, the details will be discussed in [Section 4.3.2](#).

17

18 4.3. *“In-line” rheometry*

19 In contrast to the off-line rheometry, the “in-line” (also “on-line” in some
20 literature) rheometry allows the rheological measurements in the continuation of
21 processing. This can be achieved by incorporating an instrumented die rheometer at
22 the exit of the extruder [109]. This technique avoids any subsequent structural
23 changes and water loss during another rheological measurement run.

24

1 4.3.1. *Single-channel die rheometer incorporated to an extruder*

2 In this technique, either a CDV or SDV can be directly associated with an extruder
3 similar to the set-up in an off-line extruder-type rheometer. Both Bagley method
4 [55,110,111] and pressure gradient method [53,84,112-117] have been used for
5 viscosity measurements. Different shear rates can be achieved by varying the screw
6 speed for a choke fed extruder (SSE) [2,48,95,111,113-115,118], or by varying the
7 feed rate in a starve fed extruder (TSE) [53,55,64,83,84,93,110,116,117], both of
8 which changes the throughput of the extruder. Using both CDV and SDV may
9 achieve a wider range of shear rate [84,113]. Martin et al. [84] showed that shear rate
10 ranges of $1-10^3 \text{ s}^{-1}$ and 10^2-10^4 s^{-1} could be obtained by using SDV and CDV
11 respectively.

12 Changing the throughput of extruder, however, also made the material to be
13 subjected to different thermomechanical treatments (SME and temperature) at
14 different shear rate settings. This can explain the strange results such as negative n
15 values obtained by some authors [114,119]. For twin screw extruders, this issue may
16 be addressed by controlling screw speed and feed rate simultaneously, to provide an
17 equal thermomechanical treatment during the process [117]. This, however, leads to a
18 very long and complex experimental procedure [120].

19 Many studies have shown that the operation of the in-line viscometer has a
20 considerable effect on the rheological properties of starch [24,93,111,113,117,119]
21 due to the granular transformation and macromolecular degradation. To correct these
22 effects, some authors have proposed the viscosity models involving the dependence of
23 strain history [97], SME [84], and starch conversion [113], which could be extended
24 to other systems. However, the models depending on an extrusion operating variable

1 such as screw rotation speed [93] cannot be generalised for other systems. These
2 models are detailed in [Section 5.1.6](#).

3

4 *4.3.2. Double-channel die rheometer incorporated to an extruder*

5 The main purpose of using a double-channel die (DCD) rheometer incorporated to
6 an extruder is to reduce or eliminate the interference between die measurement and
7 extruder operation. To this end, Padmanabhan and Bhattacharya [119] introduced an
8 idea of using a side-stream valve to vary the flow rate at the SDV, which has been
9 applied in a series of studies [77,78,85,121,122]. In this design, a side-stream valve
10 was placed near the exit of a SSE which was flood-fed at fixed screw speeds (cf.
11 [Fig. 4](#)). By adjusting the opening of the side-stream valve, the flow rate through the
12 slit die is controlled and the shear rate is varied. The rheological data obtained using
13 this technique (power law index $n = 0.30\text{--}0.44$ for moisture contents of 25–35%, die
14 temperatures of 160–180 °C, and screw speeds of 160–240 rpm) were significantly
15 different from those obtained by varying the screw speed, which for some conditions
16 yielded values of $n < 0$ [119]. They claimed that the side-stream valve can
17 significantly reduce the processing history effects on the rheological data and provide
18 a wide range of shear rate [119]. Similar idea has been applied with a TSE [123,124].
19 However, with this technique, it seems difficult to maintain a constant total flow:
20 when the opening of the side stream valve is increased, there is no way to decrease the
21 opening of the SDV channel. This could result in the pressure variation and thus
22 changes in the extrusion conditions.

23

24 [Insert [Fig. 4](#) here]

25

1 Based on the previously proposed principle by Springer et al. [125], an in-line
2 rheometer called “Rheopac” has been developed by Vergnes et al. [120] and used in
3 the rheological studies of starch polymer melts [58,126-129]. A schematic
4 representation of this rheometer is shown in Fig. 5. This rheometer can divide the
5 main flow of melt into two geometrically identical channels, one for the measurement
6 and the other for derivation. Each channel is provided with a piston valve, which can
7 be moved up and down to partially obstruct the flow section. It would thus be
8 possible to modify the flow rate in the first channel and to balance this variation in the
9 second channel, so that the entrance pressure remains constant. To achieve this, a
10 careful design is needed [120]. The relationship between the two valve openings is
11 determined by the n value. However, if a proper ratio between the valve and slit
12 lengths is chosen, and the n value of the melt is higher than 0.4, the dependence of
13 valve opening on the n value is weak [120].

14

15 [Insert Fig. 5 here]

16

17 As a result of such design, the Rheopac permits the variation of the shear rate in
18 the measuring section without modifying the flow conditions along the extruder, so
19 that the material undergoes the same thermomechanical history. Another great
20 advantage of this rheometer is that measurements can be performed more swiftly than
21 with a classical slit die, since no waiting time for the stabilisation of the melt flow is
22 required after adjusting the piston height for different shear rate [120]. However, it
23 has been suggested that each channel of the Rheopac is only be partially obstructed by
24 the piston since starch overcooking and die fouling would happen in case of fully
25 closed channels.

1 Li et al. [130] also used an in-line SDV for the rheological study of TPS. There
 2 was an adapter fitted between the SDV and the extruder to allow the diversion of flow.
 3 Both the flow restriction towards the bypass channel and the one towards the SDV
 4 could be controlled by two valves for each of them. By adjusting the openings of the
 5 two valves, the flow rate in the SDV was varied to achieve different shear rate.
 6 Instead of calculating the relationship between the two valve openings (which is used
 7 for the Rheopac [120]), there was a pressure transducer mounted before the two
 8 valves, which could be used to monitor and maintain the entrance pressure (P_0) at a
 9 constant value while adjusting the valve openings. Therefore, it possesses the merits
 10 of the Rheopac while it is more convenient to use.

11 Drozdek et al. [131] used a specially designed dual-orifice capillary die (cf. Fig. 6)
 12 which attached to a TSE to determine the n value of starch polymer melts. This die
 13 enables two flow rates to be collected at one extruder condition. The radii of the two
 14 capillaries are chosen so that the total cross-sectional area of the two branching
 15 capillaries is the same as the cross-sectional area of the initial capillary to reduce
 16 entrance flow effects. Each capillary has sufficient length to ensure the development
 17 of fully developed laminar flow before the exit. The die can be maintained at constant
 18 temperature for both capillaries. The power law index is then determined by the
 19 equation:

$$20 \quad n = \frac{\log\left(\frac{L_s}{L_L}\right) + \log\left(\frac{r_L}{r_s}\right)}{\log\left(\frac{Q_L}{Q_s}\right) - 3\log\left(\frac{r_L}{r_s}\right)} \quad (2)$$

21 where L , r , and Q are respectively the length, radius, and volumetric flow rate of a
 22 capillary, with the subscript “S” means the small one and “L” means the large one.
 23 This method provides a more accurate and time efficient determination of the n value

1 than any other in-line methods. However, due to the geometry restrictions, pressure
2 transducers at the entrance to the bifurcated flow channels and along these channels
3 was not possible, and therefore this rheometer was not suitable for the determination
4 of the K value.

5

6 [Insert [Fig. 6](#) here]

7

8 *4.4. Others types*

9 Some special rheometers such as multipass rheometer (MPR) and mixer-type
10 rheometer can be utilised both to process native granular starch (with plasticiser) at
11 controlled thermomechanical conditions, which simulates temperature, high-shear,
12 and high-pressure conditions in an extruder, and to evaluate their rheological
13 properties. Therefore, they represent new types of rheometers for more convenient
14 and efficient rheological study of starch polymer melts.

15

16 *4.4.1. Multipass rheometer*

17 A multipass rheometer (MPR) has recently been developed for the rheological
18 measurements of liquids and polymer melts [132-134]. Tajuddin et al. [135], for the
19 first time, used a MPR for the study of rheological properties of TPS. [Fig. 7](#) gives a
20 schematic representation of the MPR. It consists of a top and a bottom barrel in
21 which two servo-hydraulically driven pistons enter respectively. A capillary test
22 section is positioned between the barrels. The temperature of the barrels and capillary
23 can be accurately controlled, and the pressures in the barrel sections are monitored.
24 After introduction of the material, one piston will be moved toward the other until a
25 specific hydrostatic pressure is achieved. The two pistons are then synchronously

1 driven such that their separation remains constant. In “multipass steady” mode, the
2 pistons advance at constant velocity for a given time, yielding steady shear data. The
3 piston position is then held constant for a set dwell time and then the piston motion is
4 reversed. In this way, a multitude of successive steady flow measurements can be
5 made. Mean differential pressure can be calculated at certain piston speed. Bagley
6 correction can be applied by using capillaries with different L/r ratios [72]. Different
7 piston speeds are used for obtaining the result at a wide range of shear rates. Thus,
8 the viscosity can be calculated.

9

10 [Insert [Fig. 7](#) here]

11

12 Compared to other conventional rheometers, the MPR has the advantages such as
13 the requirement of only a small amount (~20 g) of sample, the pressurisation of
14 sample, and the fully closed and sealed barrels. These allow MPR to be a suitable
15 tool to measure the rheological properties of TPS.

16 Native starch (pre-blended with plasticiser) can be processed by MPR under
17 determined pressure, temperature, and processing intensity (shear rate and time) [135],
18 which can be monitored by the decrease in viscosity with time. When the viscosity
19 reached a stable value, it is considered that the sample had achieved a stable state and
20 was ready for rheological measurements. This stable state is crucial otherwise
21 molecular degradation may continue to occur during measurement.

22 As a relatively new rheometer, MPR has not been fully employed for starch
23 polymer melts. Since MPR can also be operated in an oscillatory mode [133], it could
24 provide a reliable method for studying dynamic shear viscoelastic properties.

1 Furthermore, it has also proven useful in studying viscous conditions favouring
2 bubble growth in polymer melts [136].

3

4 4.4.2. *Mixer-type rheometer*

5 It has been demonstrated that, by using an internal mixer with a closed chamber
6 (Haake Rheomix[®]), TPS can be prepared under defined thermomechanical conditions,
7 and its rheological behaviour can be monitored in real time [31,32,52,137]. The
8 mixer used in the reports has three temperature-controlled barrels. It can be
9 incorporated with different types of twin rotors such as roller rotors. The volume of
10 the chamber with the rotors is 69 cm³. The material can be loaded into the chamber
11 through a hopper on the top of the middle barrel, followed by compression and sealing
12 with a plunger. According to the manufacturer, better mixing is achieved in starved
13 conditions; however, for restraining the water evaporation and better shear treatment
14 of starch, maximum filling of the chamber need to be ensured. During measurement,
15 motor torque, barrel and material temperature are recorded as a function of time
16 [31,32,52]. Additionally, a pressure transducer can be fixed on the front part of the
17 chamber to enable the pressure measurement inside the chamber [137].

18 In some studies [31,32,52], such a mixer was used to investigate the
19 transformation of native granular starch into a thermoplastic form, which could be
20 followed by the change in torque with time. When the torque value reached a stable
21 value, it was considered that a stable state of TPS is achieved under specific
22 processing conditions (initial temperature and rotor speed). In another study [137],
23 the focus was on the rheological properties of TPS fully developed in the mixer under
24 different moisture and temperature conditions. In order to convert the torque into a
25 stress value and the rotation speed into a shear rate value, the flow curve of a well

1 characterised molten polymer was used and the empirical correlation through a
2 classical least square procedure is practised. An alternative method involves the
3 assumption of the flow in the Rheomix device to be in a double Couette system [138].
4 It has been reported that, though wide shear rate range (10–1000 s⁻¹) could be
5 obtained by Rheomix, heat generated by viscous dissipation in high shear rate range
6 can hardly be evacuated through the chamber cooling system, and this may result in
7 large discrepancies on the results [137].

8

9 **5. Processing rheology of starch polymeric materials**

10 *5.1. Steady shear viscosity*

11 Steady shear viscosity is the most prevalently measured rheological property of
12 starch polymer melts. This is because practical production requires the understanding
13 of melt flow curve of the material. Based on a scrutiny of the literature in this topic,
14 the dependence of shear viscosity of starch polymer melt on shear rate has generally
15 been considered in a power-law relationship, which can be expressed in the equation:

$$16 \quad \eta_s = K\dot{\gamma}^{n-1} \quad (3)$$

17 where $\dot{\gamma}$ is the shear rate and K is the consistency coefficient. The n value lower than
18 1 means the shear thinning behaviour of starch polymer melts, which is mainly
19 ascribed to the gradual reduction of molecular entanglement at increased shear rate.
20 The more the n value approaches 1, the more the melt behaves like a Newtonian fluid,
21 which means it is less sensitive to shear rate. Based on [Eq. 3](#), many authors have
22 focused on the effects of those formulation (plasticiser type and content) and
23 processing parameters (SME, temperature, etc.) on n and K in their studies. Thus,
24 different empirical equations describing n and K based on different systems have been
25 proposed, which are summarised in [Tab. 3](#). However, it may be difficult to make

1 direct comparisons of these models especially their constants due to the differences of
2 samples and measurement methods and conditions. Therefore, the effects of
3 thermomechanical treatment, temperature, plasticiser/additive, starch type/structure,
4 additives, and blends/composites will be discussed in detail respectively in the
5 following sections. Then, the shear viscosity models will be further discussed.

6

7 [Insert [Tab. 3](#) Here]

8

9 *5.1.1. Effect of thermomechanical treatment*

10 During processing, starch could undergo different degrees of granular
11 transformation and of macromolecular degradation under thermomechanical treatment;
12 thus, actually different products with different rheological properties may be obtained.
13 To understand the effects of processing on the shear viscous properties of starch
14 polymer melts, in-line methods have been most frequently utilised
15 [58,77,84,93,97,111-113,117,119,120,123,126,127,129-131]. Besides, pre-shearing
16 [100] and off-line rheometers [106] have also been used.

17 It has been reported that increasing the screw speed could reduce the melt
18 viscosity for both in-line [93,112,123] and offline [106] rheometric systems.
19 Particularly, when a TSE was used (shear rate was controlled by the feed rate), the
20 increase in screw speed, though reduces the degree of fill and the mean residence time,
21 increases the intensity of mechanical treatment, which results in greater granular
22 transformation and macromolecular degradation and thus lower melt viscosity; and
23 this mechanical treatment was more important at lower temperature [93]. Besides, an
24 increase in feed rate for TSE can also provide a greater thermomechanical treatment
25 due to the increase in the compression of material inside the extruder. However,

1 when the feed rate is too high, the thermomechanical energy that a specific amount of
2 material received would reduce, resulting in a lower degree of starch transformation
3 and thus higher viscosity [130].

4 In contrast to the screw speed, feed rate, SME has been much more preferably
5 used to evaluate the effect of thermomechanical treatment on the changes in starch
6 because SME can be a combined effect manipulated by the screw speed and feed rate.
7 According to the literature [93,126,129], when a TSE is used, higher screw speed (N),
8 lower feed rate (Q), or higher N/Q can lead to higher SME. Besides, screw profile can
9 also have impact on SME. The screw with more shearing and kneading elements
10 would definitely provide a greater SME during processing [106,126]. Furthermore, it
11 should be expected that different pattern of change in SME as a function of N/Q can
12 be generated when different screw profile is used. As observed by Berzin and
13 Tighzert [129], while SME was increased by increasing the N/Q ratio, the effect of
14 N/Q was more important when a more restrictive screw profile was used. However,
15 one should bear in mind that SME ($= \Gamma \times N/Q$) cannot be well defined because it
16 contains a variable (torque Γ) that is not truly independent and related to the shear
17 viscous properties of the melt [130].

18 It has been unanimously agreed that higher SME input can result in a greater
19 starch granular transformation and macromolecular degradation (as demonstrated by
20 intrinsic viscosity and SEC profile) [58,106,120,127,129], both of which lead to the
21 decreased viscosity of starch polymer melt. Martin et al. [84] observed a linear
22 relationship between K and SME in a single-logarithmic plot [Fig. 8]. However, the
23 manner in which SME influences viscous properties can be different under different
24 conditions. Using a pre-shearing rheometer for starch with 28% moisture content and
25 at 110 °C or 150 °C temperature, Vergnes and Villemaire [100] observed that, while

1 higher SME led to a lower viscosity (lower K value), the n value was not affected.
2 They also observed that the effect of thermomechanical treatment is more or less
3 marked according to the temperature [100]. In another study where a Rheopac
4 rheometer incorporated to a TSE was used, Vergnes et al. [120] reported that a
5 change in SME from 180 to 241 kWh/t by varying the feed rate can result in the great
6 changes in both K from 9050 to 2610 Pa.sⁿ and n from 0.35 to 0.52 for the TPS at
7 moisture content of 16.7% and temperature of 190 °C.

8

9 [Insert [Fig. 8](#) here]

10

11 To account for the discrepancies mentioned above, it needs to be stated that SME
12 may not be (though commonly has been) taken as the sole indication of the degree of
13 thermomechanical modification of starch polymer melt during extrusion. As observed
14 by Li et al. [130] with a DCD incorporated to a TSE, the degree of starch
15 gelatinisation, and the melt viscosity remained unchanged even though torque and
16 SME increased with the increase in screw speed at a constant degree of fill. This
17 increase in SME, however, was counterbalanced by a decrease in “specific thermal
18 energy” because residence time decreased with increasing screw speed at a constant
19 barrel temperature.

20

21 *5.1.2. Effect of temperature*

22 By using an in-line system, some authors have studied the effect of temperature
23 during processing, which can affect the changes in starch, and thus the melt viscosity.
24 For example, Li et al. [113] found that the maximum apparent viscosity occurred at
25 120–140 °C barrel temperature for all different shear rates. They suggested that the

1 increase in melt viscosity at ≤ 130 °C is due to the increase in starch gelatinisation,
2 whereas the decrease in the melt viscosity at ≥ 130 °C indicated that starch
3 degradation occurred. Here, it needs to be pointed out that, in most studies by an in-
4 line system, it is difficult to differentiate the effect of temperature on starch granular
5 transformation and macromolecular degradation and their effects directly on reducing
6 the viscosity of starch as a polymer. Furthermore, when reading the literature on the
7 in-line rheology of TPS, one should take note of what kind of temperature was used as
8 a varied parameter: the temperature at the last barrel zone(s) and die (processing
9 temperature) [93,112,119,130], or the melt temperature at the die channel (testing
10 temperature) [58,84,113,120,127,129,131]. In the former case, the melt temperature
11 may be higher than the controlled temperature because of the viscous dissipation
12 (discussed in [Section 5.4](#)). Thus, misleading rheological results may be generated. In
13 the latter case, it was common to achieve different desired melt temperatures by
14 varying the temperatures of barrel zones and die, of which the details, however, were
15 often missing. On the other hand, it is a remarkable that, even if an off-line system is
16 used, the temperature of the second measurement run may still have some
17 “processing” effect. Willett et al. [108] indicated that, when the measurement
18 temperature was high (160 or 180 °C), significant macromolecular degradation could
19 occur during the testing phase, to the point that any effects of starting materials were
20 eliminated.

21 In the following in this section, the temperature effect on melt viscosity in terms
22 of thermal activation of melt flow will be discussed. It is well known that an increase
23 in temperature would result in a lower viscosity of starch polymer melt. According to
24 [Eq. 3](#), this can be reflected by a lower value of K at higher temperature as widely
25 reported in the literature [40,44,49-51,58,65,84,90,91,94,100,106-108,110,113-

1 116,118,120,122,127,129,135,137,139]. However, there have been discrepancies
2 over the effect of temperature on the n value. In some especially early studies
3 [99,108,110,113,114,116,118,129,137,139], the n was assumed to be a constant in the
4 shear viscosity models; thus, the effect of temperature on n was not elaborated. By
5 drawing the shear viscosity versus shear rate curve in a double-logarithmic plot, other
6 researchers observed that an increase in temperature would cause a higher n value
7 [58,65,94,100,107,115,122,127,135]. The same trend has been observed for
8 starch/PLA blends [49-51]. In the meantime, there have been reports showing that no
9 clear influence of temperature on n for starch polymer melts [44,84].

10 The relationship between temperature and n may be complex when starch is
11 plasticised with different plasticisers and/or blended with other materials. Yu et al.
12 [40] studied the shear viscous properties of TPS plasticised with 30% glycerol content
13 without or with the addition of citric acid (1 or 3%). The results indicated that, while
14 temperature from 130 to 150 °C slightly increased the n value without or with 3%
15 citric acid, there was an apparent reverse trend for TPS with 1% citric acid. By using
16 the same TPS samples but blended with low linear density polyethylene (LLDPE),
17 Wang et al. [91] found that, when temperature increased from 130 to 150 °C, the n
18 value decreased for the blend without citric acid, but first increased and then
19 decreased for the blends with 1 and 3% citric acid. In another study by Ma et al. [90],
20 while an increase in temperature from 110 to 130 °C led to a great increase in n value
21 for TPS plasticised by formamide and urea mixture, a decrease in n with increasing
22 temperature was observed for the same sample but filled by 10% fly ash. The authors
23 didn't further analyse these phenomena however. It could be possible that shear
24 viscous properties are complicated by the chemical reactions and/or molecular

1 interactions among starch, plasticiser, and the other polymer. This will further be
2 discussed in the following sections.

3

4 *5.1.3. Effect of plasticiser/additive*

5 Plasticisers usually have a large influence on the shear viscous properties of starch
6 polymer melts. In most cases, plasticiser is blended into native granular starch before
7 processing. As a result, the plasticiser content would not only influence the granular
8 transformation and macromolecular degradation during processing, which affect the
9 viscosity, but also assist the movements between starch inter- and intra- molecular
10 chains, which reduce the viscosity as well. Particularly, Willett and co-workers
11 [65,108] was able to separately determine the effects of moisture content during
12 processing and during measurement by using an off-line system. In one study [108],
13 starch was pelletised at different moisture contents during the first run and then
14 equilibrated to the same moisture content for shear viscosity measurements. It was
15 shown that moisture content during the pelletising step had a significant impact on
16 melt viscosity when tested at low temperature (110 or 130 °C): the TPS sample
17 pelletised with 15% moisture content had the lowest viscosity, that pelletised with
18 20% moisture content had the highest, while that pelletised at 30% moisture content
19 had an intermediate value. The reasons could be that the high melt viscosity (during
20 processing) at 15% moisture content caused more shear stress and more chain scission,
21 while water catalysed hydrolysis might occur with high moisture content (30%). In
22 the other studies [65,108], TPS pellets were prepared at the same moisture content and
23 subsequently equilibrated them to different moisture contents for shear viscosity
24 measurements.

1 Apart from the effect on starch granular transformation during processing, an
2 increase in plasticiser content would decrease the viscosity of starch polymer melt
3 since it can decrease the polymer entanglement density and increase the ease of
4 disentanglement. It has been well demonstrated that a higher amount of water would
5 result in a lower K value [57,58,65,84,93,94,99,100,107,108,110,111,113-
6 119,122,127,129,137,139,140]. However, the effect of moisture content on the n was
7 unknown in many studies since it was taken as a constant for modelling
8 [57,93,99,110,113,114,116-119,129,137,139,140]. In other reports where the n values
9 were shown at different moisture content, an increase in n with increasing moisture
10 content was mostly observed [58,65,94,100,107,111,115,127] although there have
11 also been reports where no evident trend of n with the change in moisture content
12 could be justified [45,84,122,131].

13 As a frequently used plasticiser for starch, glycerol reduces the viscosity of starch
14 polymer melts as evidenced by a lower K value [41,106]. The impact of glycerol
15 content on n , however, has been in disagreement especially based on the limited
16 published data. While Thunwall et al. [96] reported an unchanged n value with
17 increasing glycerol content for hydroxypropylated oxidised potato starch, Rodriguez-
18 Gonzalez et al. [41] observed a higher glycerol content slightly reduced the n value
19 for wheat starch. Regarding the latter result, it could be possible that when the
20 glycerol content is lower, less degree of starch granular transformation occurs during
21 processing, and the remnant large amount of starch granules make the fluid behave
22 more like a filled polymer melt. As a result, higher n value is displayed. Otherwise, a
23 higher n value should be expected with increasing glycerol content, and this has been
24 verified through rheological modelling [84,135].

1 By MPR, Tajuddin et al. [135] investigated the shear viscous properties of well
2 transformed waxy TPS melts plasticised by both water and glycerol. The results
3 showed that an increase in glycerol/water ratio (1:4, 2:3, and 3:2) resulted in a
4 stronger shear-thinning behaviour; however, total plasticiser content (70–110%) had
5 little influence on n (cf. Fig. 9). It was thus proposed that, different structural
6 characteristics can result with different plasticiser (cf. Fig. 10): when plasticised
7 mainly by water, amylopectin molecule has a compact ellipsoidal conformation by
8 greatly unfolding their branches, and these “ellipsoids” are easy to move, so more
9 Newtonian-like behaviour is shown; the “ellipsoids”, however, are largely absent
10 when glycerol is the main plasticiser, and the amylopectin molecules behave more
11 like a standard polymer and show stronger shear-thinning behaviour.

12

13 [Insert Fig. 9 here]

14 [Insert Fig. 10 here]

15

16 Many other low molecular weight substances such as citric acid, formamide, and
17 urea have also been utilised as plasticisers for starch. Citric acid can form stronger
18 hydrogen bonding interactions with starch molecules than glycerol [40]. It weakens
19 the interaction of starch molecules and improves the plasticisation of starch [91].
20 Further, it may also depolymerise starch molecules during processing [49]. As a
21 result, citric acid can obvious reduce the viscosity of starch polymer melts, though its
22 effect on n has not been well understood [40,49,91]. On the other hand, plasticisers
23 such as formamide and urea are also effective plasticisers since their amide groups
24 enable them to form strong hydrogen bonds with starch and to break the existing
25 hydrogen bonds in starch [44,90,92]. Such strong interaction allows formamide to be

1 used to plasticise starch even without water [51,92]. Wang and co-workers [51,92]
2 examined the effect of formamide/glycerol ratio on the shear viscosity of TPS at fixed
3 total plasticiser content, and showed that an increase of formamide/glycerol ratio
4 decreased the K value but increased the n value. Nevertheless, when 30% (dry basis)
5 of the mixture of formamide and urea was used as plasticiser, TPS could have a
6 higher shear viscosity and a lower n value than that plasticised by the same amount of
7 glycerol [90]. In another study, with the increase of formamide-urea mixture from 30
8 to 50%, the n value first decreased and then increased [44]. Considering the whole of
9 the mixture plasticiser could be effectively bound to starch at 40% level [44], it can be
10 considered that, before 40%, the increase of plasticiser content resulted in more
11 hydrogen bonds which reduced the “ellipsoids” in starch and cause a stronger shear
12 thinning behaviour (cf. [Fig. 10](#)); however, when the plasticiser content was higher
13 than 40%, the excess of plasticiser reversed the trend due to its Newtonian behaviour.
14 Moreover, the authors of all these studies have shown that the use and higher content
15 of formamide, urea, and/or citric acid comparing with glycerol could generally cause
16 a decrease in flow activation energy (E/R , cf. [Eq. 4](#) in [Section 5.1.6](#)), indicating less
17 temperature-sensitivity of TPS plasticised by these plasticisers [40,44,49,51,90-92].

18 Willett et al. [108] investigated the effects of various low molecular weight
19 additives such as urea, lecithin, triethylene glycol (TEG), glycerol monostearate
20 (GMS), and polyoxyethylene stearate (POES) on the shear viscosity of TPS, and the
21 results are summarised in [Tab. 4](#). It was found that all additives except GMS
22 significantly lowered the melt viscosity of TPS, with lecithin and POES exhibiting the
23 greatest efficiency (decreasing K and increasing n), though lecithin could effectively
24 reduce the molecular degradation of starch as well. Relative to the melt with 15%
25 moisture content, all the additives except GMS were more effective than additional

1 water at reducing viscosity, which can be ascribed to the strong interactions between
2 these additives and starch molecules. The melt viscosity with GMS was essentially
3 the same as, or slightly higher than, those of starch/water, and this behaviour could be
4 attributed to the presence of unmelted amylose–lipid complexes in the melt. Though
5 amylose–lipid complexes could also form in the samples plasticised by lecithin and
6 POES, they were most likely melted at the testing temperature (160 °C) and thus had
7 no apparent effects on the rheological results.

8

9 [Insert [Tab. 4](#) here]

10

11 Yu et al. [141] found that the addition of 10% urea, glycerol, sugar, KI, or NaCl to
12 TPS containing 30% moisture content was not as efficient as increasing the moisture
13 content from 30% to 40% in decreasing the viscosity. These results suggest that these
14 additives have weaker capacity to form hydrogen bonds with starch and to facilitate
15 starch molecular movements than water.

16 Supercritical carbon dioxide (sc-CO₂), which has been considered as a novel
17 plasticiser in extrusion processing [142], also has an impact on the rheological
18 properties of starch polymer melts. Recently studies [124,143] have shown that the
19 use of sc-CO₂ during extrusion processing lead to a lower K and a higher n for TPS
20 melt. This is because sc-CO₂ can solvate starch molecules and reduce polymer
21 entanglement and subsequently decreased shear-thinning behaviour and viscosity. As
22 a result, sc-CO₂ has a great potential for improving the processibility of starch
23 polymer melt.

24 Though a lubricant is an important additive in practical processing of starch
25 polymers, there have been few studies dealing with the effect of lubricant on the shear

1 viscous properties of starch, expect that Thuwall et al. [43] showed that the addition
2 of 3% fluoride elastomer lubricant to glycerol-plasticised amylose-rich potato starch
3 had no significant effect on melt viscosity.

4

5 *5.1.4. Effect of starch type/structure*

6 By using pre-shearing rheometer, Della Valle et al. [103] have shown the
7 difference of rheological properties of TPS melts from different botanical origins. For
8 example, smooth pea and wheat starches have the same n value, which is slightly
9 higher than that of potato starch. By rheological modelling, they also showed that the
10 shear viscosity of smooth pea starch has a greater dependence on temperature than
11 any other types. On the other hand, starches with different amylose/amylopectin
12 ratios but from the same botanical origin have attracted particular scientific interests
13 as they display different processing and product properties. Previous studies [42,144-
14 153] have shown that polymeric materials based on high-amylose starch exhibit
15 superior strength and toughness; however, the extrusion processing of high-amylose
16 starch is much more difficult than that of low-amylose starch, partly due to the higher
17 die pressure and torque requirements as results of the higher melting temperature and
18 viscosity of the former [23,154,155]. Della Valle et al. [127] and Xie et al. [107]
19 systematically investigated the shear viscous properties of maize starches with
20 different amylose/amylopectin ratios and both groups found that the higher the
21 amylose content, the higher is the shear viscosity and the more pronounced is the
22 shear-thinning behaviour, under the same shear rate range (Fig. 11). This is also the
23 case for potato starch [43] and wheat flour [98]. As discussed before, amylopectin
24 mainly has clusters composed of short chain branches ($DP \approx 15$); and, despite its high
25 molecular weight, it has a compact ellipsoidal conformation which reduced its ability

1 to create entanglements, resulting in a lower viscosity [107,127]. In contrast, the long
2 linear chains of amylose cause more entanglements between macromolecules, which
3 increases zero shear viscosity and enhanced non-Newtonian behaviour. In addition,
4 the high viscosity of high-amylose starch can also be attributed to its lower tendency
5 to undergo granular transformation [23] and macromolecular degradation [66].

6

7 [Insert [Fig. 11](#) here]

8

9 Chemically modification may also have some influence on the viscous properties
10 of starch polymer melts because the modified groups may impact the interaction
11 between starch molecular chains. Thunwall et al. [96] observed a lower viscosity and
12 higher n value for hydroxypropylated and oxidised potato starch compared to those of
13 normal potato starch. This may be ascribed to the reason that chemical modification
14 weakens the starch intra- and inter-molecular interactions and facilitates the formation
15 of “ellipsoids”, which results in more Newtonian behaviour. However, Berzin et al.
16 [129] claimed that wheat starch, after cationisation, showed little difference in shear
17 viscosity.

18

19 *5.1.5. Effect of blending/compositing*

20 Generally, blending starch with another polymer would produce an average
21 viscosity. This has been measured in the starch-based blends mostly with PCL
22 [53,54,89], PLA [49,50,52], and PVA [56,57] as well as with other synthetic polymers
23 [105]. It should be noted that, in some studies [49,50,52-54,57,89], the viscosity of
24 TPS was higher than that of the second polymer phase, while a reverse pattern was
25 observed in other studies [47,51,56]. This largely depends on the measurement

1 temperature and the plasticiser(s). For example, Xie observed that an increase in
2 starch/PLA ratio could increase the viscosity of the blend at temperature of 180 °C,
3 whereas Sarazin et al. [47] found that adding starch (with 24 or 36% glycerol content)
4 to PLA could reduce the viscosity of PLA at temperature of 165 °C. The influence of
5 blending on the n value follows the same pattern. Since the n value of TPS is usually
6 lower than that of the second polymer used due to its stronger shear-thinning
7 behaviour, blending usually results in a higher n value [49,50,52,57]. However, care
8 should be taken when explaining the viscous results of starch-based blends since other
9 more factors can also affect the viscosity of the blends. For instance, Wang and co-
10 workers [49,50] found that the K value of starch/PLA was even lower than both those
11 of TPS and PLA. They suggested the reason to be the depolymerisation effect of
12 citric acid (which, along with glycerol, was used as plasticiser for TPS) for both starch
13 and PLA in the blend. In another study, Wang et al. [51] discovered that there were
14 large differences in the K and n values of starch/PLA blends without or with water as
15 one of the plasticisers. With 10% moisture content in addition to formamide and
16 glycerol, the blend showed a lower K and a higher n . The n value of starch/PLA
17 blend with water was even higher than that of pure PLA. This may due to the
18 molecular weight degradation of PLA during processing with the presence of moisture
19 in starch.

20 Kalambur and Rizvi [89] studied the shear viscous properties of TPS/PCL blends
21 prepared by both standard extrusion blending and reactive extrusion (REX) blending.
22 By the latter method, added were hydrogen peroxide (H_2O_2), which help the cross-
23 linking between starch and PCL molecules, and nanoclay (Nanocor[®] I.30E
24 organoclay), which reinforced the composite. They found lower n and K values for
25 reactive blended sample compared with that of normally blended sample. This was

1 attributed to the depolymerisation of starch molecules by oxidation reactions. They
 2 also observed that an increase in nanoclay content could increase the K value or shear
 3 viscosity at low shear rates. A similar result of K was found by Ma et al. [90] who
 4 investigated the effect of the addition of fly ash into TPS on the shear viscosity of the
 5 composite. However, both studies didn't show a clear trend of the effect of the filler
 6 content on the n value.

7

8 5.1.6. Shear viscosity models

9 The relationships between different conditions and K have been described by the
 10 empirical equations listed in Tab. 3. While the earliest classical model proposed by
 11 Harper et al. [140] only includes the influences of temperature and moisture content,
 12 the latest model [84,135] also covers the effects of glycerol and SME:

$$13 \quad K = K_0 \exp\left(\frac{E}{RT} - \alpha MC - \alpha' GC - \beta SME\right) \quad (4)$$

14 where MC is the moisture content; GC is the glycerol content; T is the temperature;
 15 E/R is the reduced flow activation energy (in Kelvin); and K_0 , α , α' , and β are
 16 coefficients. This equation can be also expressed in another form:

$$17 \quad K = K_0' \exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \alpha(MC - MC_0) - \alpha'(GC - GC_0) - \beta(SME - SME_0)\right] \quad (5)$$

18 with T_0 , MC_0 , GC_0 , and SME_0 as reference conditions. In addition, some models
 19 consider screw speed [93] during processing as well; however, they are not widely
 20 utilised since the impact of the screw speed largely depends on the machine
 21 characteristics and can be more easily be reflected by SME. Though the degree of
 22 starch transformation (which can be measured by iodine or differential scanning
 23 calorimetry (DSC) method), has also been introduced into the model by some authors
 24 [113], it is actually not an operating term and thus the resulting model has poor

1 applicability in practical processing. Besides, no simple relationship between starch
 2 transformation and shear viscosity should be expected and further study is needed
 3 [31,32].

4 Some authors [106,113] suggested that the coefficients in Eq. 4 and 5 also
 5 depends on other variables (cf. Tab. 3). However, the use of such an expression has
 6 so far been limited to where only temperature and either moisture or plasticiser
 7 content were changed.

8 By an analogy with a suspension of solid particles (residual granular starch) in a
 9 fluid (molten starch), Barron et al. [102] used the hard sphere suspension model
 10 developed by Krieger and Dougherty [156] and generalised by Quemada [157] to
 11 calculate the K value:

$$12 \quad K = K_0 \left(1 - \frac{\Phi}{\Phi_m} \right)^\alpha \quad (6)$$

13 where Φ is the volumetric fraction of residual granule fragments defined as $\Phi = 1-x$
 14 with x being the degree of transformation of starch, and Φ_m is the maximum Φ value.
 15 The lower the x value, the higher is the viscosity. In this study, Φ_m was supposed to
 16 have a maximum value of 0.74 (the theoretical value for the Face Centred Cubic
 17 packing), and α was considered to be -2.5 for concentrated suspensions [102].

18 Generalised from the literature [58,100,127,135], the power-law index n can be
 19 expressed by an empirical polynomial equation:

$$20 \quad n = n_0 + \alpha_1 T + \alpha_2 MC + \alpha_3 GC + \alpha_4 SME + \alpha_{12} T \cdot MC + \alpha_{13} T \cdot GC + \alpha_{14} T \cdot SME + \\ 21 \quad \alpha_{23} MC \cdot GC + \alpha_{24} MC \cdot SME + \alpha_{34} GC \cdot SME + \alpha_{123} T \cdot MC \cdot SME + \alpha_{124} T \cdot MC \cdot SME + \\ 22 \quad \alpha_{134} T \cdot GC \cdot SME + \alpha_{234} MC \cdot GC \cdot SME + \alpha_{1234} T \cdot MC \cdot GC \cdot SME \quad (7)$$

23 where n_0 and α are constants. Actually, not all of these parameters (T , MC , GC , and

1 *SME*) were used in a single study in literature, so the reported models were actually
 2 simpler.

3 With values of K and n calculated by Eq. 4–7, the shear viscosity (Eq. 3) at
 4 specific conditions can be predicted. In practice, Eq. 4, 5 and 7 may need to be varied
 5 depending on the sample and the measurement method and conditions. For example,
 6 if another plasticiser is involved, one more term regarding that plasticiser need to be
 7 used. Furthermore, based on the constants in these two equations, we could determine
 8 which variables are significant while others have little influence.

9 Though the power-law model has been predominantly used for starch polymers,
 10 the existence of a yield stress in a shear stress versus shear rate plot has been shown in
 11 some studies [95,103]; thus, the shear viscous behaviour could be described using
 12 Herschel-Bulkley relationship:

$$13 \quad \eta_s = \frac{\tau_0}{\dot{\gamma}} + K\dot{\gamma}^{n-1} \quad (8)$$

14 where τ_0 is the yield stress. The existence of a yield stress generally indicates a
 15 structuration of the material. For starch polymers, this may be attributed to the
 16 recrystallisation of starch at rather low shear rate [103].

17 Mackey and Ofoli [97] employed a more comprehensive model involving
 18 correction for $\dot{\gamma}$, T , MC , time-temperature history (ψ), and strain history (ϕ) for
 19 predicting the shear viscosity of starch polymer melt processed by a twin-screw
 20 extruder:

$$21 \quad \eta_s = \left[\left(\frac{\tau_0}{\dot{\gamma}} \right)^{n_1} + \mu_\infty \dot{\gamma}^{n_2 - n_1} \right]^{\frac{1}{n_1}} \exp \left[\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + b(MC - MC_0) \right] \cdot \left[1 + A(1 - e^{-k\psi})^\alpha \right] \cdot \left[1 - \beta(1 - e^{-d\phi}) \right]$$

22 (9)

23 where the constants are $\tau_0 = -1.89 \times 10^5$, $n_2 = 0.979$, $n_1 = 0.356$, $\mu_\infty = 6.93 \times 10^4$ Pa·s; $k\psi$
 24 $= \infty$ (indicating very rapid gelatinisation); and $d = -5.87 \times 10^8$; and the reference

1 conditions are $T_0 = 323.15$ K, $MC_0 = 0.476$ (dry basis). The other parameters can be
2 calculated by:

$$3 \quad \alpha = \exp\left(18.9 - \frac{6070.6}{T}\right) \quad (10)$$

$$4 \quad \beta = \exp\left(-6.371 + \frac{2530.5}{T}\right) \quad (11)$$

$$5 \quad A = \beta(C_s)^\alpha \quad (12)$$

6 where C_s is starch concentration (wet basis). The second last term in Eq. 9 represents
7 the corrected time-temperature history, considering the effects of temperature and
8 moisture content on the gelatinisation kinetics. The last term in Eq. 9 stands for the
9 corrected strain-history, taking into account of total shaft power of the TSE. Thus, it
10 can be considered relating to SME. Nevertheless, the authors suggested that the
11 model needs to be further improved by better quantifying the strain history and time-
12 temperature effects [97].

13 Finally, it is important to note that, the Carreau-Yasuda model, though has been
14 used for many standard polymers, has not been used for starch polymer melts. The
15 equation of this model is:

$$16 \quad \eta_s = \frac{\eta_0}{\left[1 + (\lambda\dot{\gamma})^a\right]^{\frac{1-n}{a}}} \quad (13)$$

17 where η_0 is the shear viscosity at zero shear rate, λ is the relaxation time (s), and a is
18 the Carreau-Yasuda fitting parameter. The use of this model for starch polymer melts
19 may help in understanding the influence of shear rate on starch structures.

20

21 5.2. Steady extensional viscosity and first normal stress difference (elasticity)

22 Starch polymer melts are commonly considered to exhibit a viscoelastic behaviour.

23 The measurement of elastic component of a starch polymer melt can be associated

1 with the extensional viscosity (η_e) and the first normal stress difference (N_1).
2 Compared to shear viscosity, η_e and N_1 have received minimum attention. The
3 difficulty in their measurement may be part of the reasons [68]. Nevertheless, the
4 study of elasticity of starch polymer melt is crucial due to several reasons:

- 5 • Extensional flow is indeed present due to the contraction at the die entrance in
6 extrusion; forces are not only put onto the material due to shear flow, but also to
7 extensional flow.
- 8 • N_1 and η_e are far more sensitive than shear viscosity to the changes or differences
9 in melt microstructure [81,158,159].
- 10 • Extensional flow function can also be used to adjust the processing conditions to
11 maintain product performances (e.g. forming [160,161]).
- 12 • Extensional flow need to be used to develop and test a “complete” constitutive
13 equation that can be used in modelling the processing operations.

14 The second point listed above has been emphasised by Seethamraju and
15 Bhattacharya [121] who found that, though the addition of 5% of salt and sugar to
16 maize grits during extrusion affected all of η_s , η_e , and N_1 (as a result of different
17 degree of gelatinisation), η_e and N_1 were more sensitive to the addition of ingredients
18 than η_s . Furthermore, the highest first normal stress difference was observed with the
19 addition of salt, while the addition of sugar resulted in the highest extensional
20 viscosity [121]. In an earlier study, Bhattacharya [162] found that the addition of
21 gluten to wheat flour dough could greatly decrease both η_e and N_1 .

22 Though it has been found in several studies [85,121,162] that the N_1 generally
23 increased with shear rate ($\dot{\gamma}$), no accurate relationship between N_1 and $\dot{\gamma}$ has
24 established for starch polymer melts. On the other hand, it has been assumed that the
25 power-law dependence of η_e on extensional rate $\dot{\epsilon}$ is applied to starch polymers

1 [78,95,121,122,162]:

$$2 \quad \eta_e = S\dot{\epsilon}^{t-1} \quad (14)$$

3 where t is power-law index and S is the consistency coefficient. As a result, starch
4 polymer melts are regarded to display an extension-thinning behaviour. However, it
5 is worth noting that, if severe extension thinning behaviour (flow behaviour index \ll
6 0) is observed, the molecular degradation under extensional flow [77] occurs since
7 extensional flow is classified as a strong flow [163]. This is more likely to happen at
8 lower moisture content [77,122]. Therefore, it is important to minimise molecular
9 degradation for obtaining accurate results of extensional viscosity of starch polymer
10 melts.

11 Like shear viscosity, η_e can be affected by different processing conditions. It has
12 been observed that increasing moisture content and temperature decreased η_e at higher
13 $\dot{\epsilon}$ [78,122]. In addition, processing history could greatly influence η_e [122].
14 However, no modelling work has been done in this aspect.

15 As t in Eq. 14 is the ratio of the rate of shear energy dissipation to that of
16 extensional energy dissipation [76], a small value of t observed for maize meal dough
17 corresponds to the dominance of extensional flow over the shear component [77].
18 The Trouton ratio, T_r , which is the ratio of the extensional viscosity to the shear
19 viscosity, is more commonly used to evaluate the elasticity of a material. According
20 to Jones et al. [164], in uniaxial extensional flow, T_r can be expressed as:

$$21 \quad T_r = \frac{\eta_u(\dot{\epsilon})}{\eta_s(\sqrt{3}\dot{\epsilon})} \quad (15)$$

22 where η_u is uniaxial extensional viscosity. And, in planar extensional flow, it can be
23 expressed as:

$$24 \quad T_r = \frac{\eta_p(\dot{\epsilon})}{\eta_s(2\dot{\epsilon})} \quad (16)$$

1 where η_p is planar extensional viscosity. In uniaxial extensional flow, $T_r = 3$ is
2 displayed for inelastic non-Newtonian fluids, and $T_r > 3$ for viscoelastic fluids; in
3 planar extensional flow, this critical value is 4. As reported by Bhattacharya et al. [78]
4 for maize meal in uniaxial extensional flow, the T_r values ranged from 25 to 50, as
5 affected by moisture content, barrel temperature, and deformation rate, clearly
6 demonstrate that the extensional viscosity is much higher than the shear viscosity;
7 thus, a significant elastic behaviour was confirmed. Seethamraju et al. [105] reported
8 an increase in starch content in starch/ethylene propylene maleic anhydride (EPMA)
9 blend from 60 to 70% resulted in a higher T_r , again suggesting a stronger elastic
10 property of starch polymer melt.

11 Finally, it is noteworthy that strain hardening (an increase in the slope of η_e versus
12 time curve above a specific strain rate) is an important property in processing like film
13 blowing and stretching. A previous study on low density polyethylene (LDPE) has
14 shown that strain hardening can be generated by long-chain branching or by
15 introducing high molecular weight components [165]. However, no studies on the
16 relationship between starch structure and strain hardening property of starch polymer
17 melt have been found.

18

19 5.3. *Dynamic shear rheology*

20 Dynamic shear rheology is another way to characterise the viscoelastic properties
21 of a material. However, due to some difficulties (especially as a result of water
22 evaporation), few reports have used this method for starch polymers. In a study by
23 Della Valle and Buleon [88], the linear viscoelastic behaviours of TPS samples from
24 various origins produced by twin-screw extrusion were studied by parallel plate
25 rheometers in oscillatory mode at 90 and 150 °C. At low strain, the plasticised starch

1 is found to behave as a viscoelastic gel-like material. This behaviour is partially
2 explained by its semicrystalline structure due to the presence of single-helical amylose
3 structures (similar to the one formed by amylose–lipid helical complexes) formed
4 after extrusion, as evidenced by X-ray diffraction (XRD) results. Crystallites are
5 assumed to participate in the formation of an elastic network, embedded in a
6 viscoelastic amorphous phase. The higher molecular weight of the potato starch is
7 responsible for its larger moduli. In the case of maize starch, the highly branched
8 amorphous amylopectin softens the structured behaviour, resulting in lower moduli
9 compared to those of rich-content amylose.

10

11 5.4. *Viscous heat effects*

12 Viscous heat effects are addressed here since they are also helpful in
13 understanding processing rheology. Further, in a REX process, melt temperature is an
14 important factor affecting reaction pathways and materials properties. Viscous heat
15 dissipation can be affected by the rheological state, and in turn impact the rheological
16 properties. Lai and Kokini [115] estimated the viscous heating for maize starch with
17 different amylose content as functions of extrusion temperature, moisture content, and
18 screw speed. They found that the temperature rise due to viscous heating decreased as
19 temperature, moisture content, and screw speed increased, which is due to rheological
20 changes in starch during extrusion. Under the same extrusion conditions, high-
21 amylose starch (Hylon 7) gave a higher temperature rise due to viscous heating than
22 low-amylose starch (Amioca), which is attributed to the larger viscosity of the former.
23 The temperature rise can be significantly reduced by using as thin a slit as possible.

24 Viscous dissipation can be given by the equation [166]:

$$25 \quad q_v = K\dot{\gamma}^{1+n} \quad (17)$$

1 where q_v is the dissipation in power per unit volume. Therefore, it can be seen from
2 Eq. 17 that both higher values of K and n can contribute to larger melting temperature
3 rise for a given shear rate, and temperature rise increased with shear rate. Based on
4 the rheological results reported by Xie et al. [107] and the specific heat capacity
5 values reported by Tan et al. [167], it can be calculated that the temperature rise of
6 maize starch could be up to 50 °C during processing without cooling.

7

8 5.5. *Controlling the processing rheology*

9 By understanding the processing rheology and by adjusting different formulation
10 and operating conditions such as plasticiser content and temperature, the processibility
11 of starch polymeric materials can be controlled. For example, Willett et al. [108]
12 showed that starch samples which were processed with 15% moisture content and
13 then conditioned to 15–20% moisture content exhibited melt viscosities similar to that
14 of LDPE with melt index of 1.8 at 160 °C. In another study, the TPS samples with
15 20% moisture content and 32% glycerol content (wet basis) also showed a viscosity
16 approaches to that of LDPE at 150 °C [41]. Moreover, with the use of rheological
17 models, the processing rheology can be further understood since the significance of
18 each variable is quantified. In this way, it could be found, for instance, that the melt
19 viscosity of TPS plasticised by glycerol is more sensitive to temperature than that by
20 formamide [92], and that the melt viscosity of waxy maize starch is more affected by
21 moisture content compared to that of high-amylose maize starch [127].

22 Shear rate is another important variable to manage the rheological properties of
23 starch polymeric materials. As reported by Kalambur and Rizvi [89], at temperature
24 of 120 °C, the shear viscosity of starch/PCL blend could be lower than that of pure
25 PCL at shear rate higher than 25.2 s⁻¹. Another report [48] demonstrated that, when

1 the shear rate was higher than 10^4 s^{-1} , the shear viscosity of TPS could be reduced
2 lower than that of PLA at 130 °C. Furthermore, Walia et al. [55] plotted the changes
3 in viscosity ratios of TPS and PHEE as a function of shear rate at different moisture
4 and temperature conditions (cf. Fig. 12). The viscosity ratio was found to vary over
5 two orders of magnitude (0.1–10) with the changes in TPS moisture content (15–30%)
6 and temperature (120–160 °C). This information could be used to understand the
7 compatibility of their blend (further discussed in Section 6.1). In practice, shear rate
8 is mostly related to the screw configuration, screw speed, and die geometry in
9 extrusion processing. As a result, increasing screw speed of the extruder may be an
10 effective way to alleviate the problems of the high motor torque and the blockage of
11 starch polymer melt in the extruder and die channels.

12

13 [Insert Fig. 12 here]

14

15 **6. Rheology-processing/product property relationships for starch polymeric** 16 **materials**

17 *6.1. Rheology-blend compatibility/morphology relationship*

18 When considering the blending of two polymers, a practical method is to first
19 compare their rheological properties. If the rheological properties of two polymers
20 differ greatly, intimate mixing and good compatibility should not be expected. Of
21 course, differences in thermodynamics and polarity of starch and the second polymer
22 must also be considered. Often the highly hydrophilic nature of starch is in contrast to
23 the hydrophobicity of the blended polymer, and thus a compatibilising strategy
24 usually has to be employed [2].

1 A change in compatibility of the blend can be reflected by the change in melt
2 viscosity. It has been shown in several studies [47,49,51,91] that a higher
3 compatibility of starch/PLA blend, which was achieved by plasticiser strategy and
4 demonstrated by a well blended morphology and better dispersion of the phases as
5 observed by scanning electron microscopy (SEM), could be reflected by a lower K
6 value and a higher n value. This is also the case for starch/PE blend [91]; and the
7 same relationship was displayed when the compatibility of starch/PLA was achieved
8 by REX [50]. Xie and co-workers [52,54] investigated the effect of compatibiliser
9 (methylenedipheny diisocyanate, MDI) distribution on the rheological properties of
10 TPS/polyester blends. The polyesters used were PCL, PLA, and PBSA. It was shown
11 that MDI did not clearly affect the viscosity of starch/polyester blends when it was
12 distributed in starch phase. However, MDI increased the melt viscosity and decreased
13 the n value of the blends when it was distributed in polyester phase. This could be
14 linked to the improved compatibility between TPS and polyester as demonstrated by
15 the improved interface in SEM results and the closer melting temperatures of each
16 phase in DSC results. They claimed that controlling the MDI distribution can greatly
17 reduce the consumption of the highly reactive isocyanate group in MDI by the
18 moisture in starch, and thus improve the compatibilising functionality of MDI.

19 Walia et al. [55] discovered that the viscosity ratio of TPS and poly(hydroxy ester
20 ether) (PHEE), which could be controlled by moisture content of TPS and temperature,
21 had a substantial effect on the size of dispersion, the type of morphologies developed,
22 and the onset and nature of continuity of the starch phase in their blends.

23 Deformation (in the flow direction) of the dispersed starch phase was possible under
24 high moisture conditions (lower viscosity ratio), leading to fibrillar and laminar types
25 of morphologies at 50–80% starch level, whereas processing at a low moisture level

1 (higher viscosity ratio) produced a more dispersed morphology. When the viscosities
2 of the two phases were significantly different, the low-viscosity polymer migrated to
3 the surface. Hence, controlling the plasticiser level and temperature can be an
4 effective way to tailor the morphology and properties of the blends.

5 A simple arithmetic relation was used by B elard et al. [53] to evaluate the
6 compatibility of starch/PCL blend. The shear viscosity (η_{exp}) of the blend was
7 measured by a SDV incorporated to a SSE according to regular procedure. Knowing
8 the shear rate during extrusion, the viscosities of both components (η_{TPS} and η_{PCL})
9 could be determined using empirical power-law model and Carreau-Yasuda model
10 respectively. The log-additive mixing rule was then used to predict a theoretical value
11 (η_{add}) of the blend viscosity according to the following equation:

$$12 \log \eta_{\text{add}} = \Phi_{\text{PCL}} \cdot \log \eta_{\text{PCL}} + \Phi_{\text{TPS}} \cdot \log \eta_{\text{TPS}} \quad (18)$$

13 where Φ_{PCL} and Φ_{TPS} are the volumetric fractions of PCL and TPS in the blend
14 respectively. The deviation of experiment value with respect to the predicted value
15 could then be calculated by:

$$16 \text{dev} = (\eta_{\text{add}} - \eta_{\text{exp}}) / \eta_{\text{add}} \times 100 \quad (19)$$

17 where the higher the deviation value is, the less compatible were the blends. However,
18 when using this method, one has to note that the molecular weight degradation of the
19 polyester during processing may also cause the decrease in η_{exp} [48], which enlarges
20 the deviation value.

21

22 6.2. Rheology-expansion/foaming property relationship

23 The rheological properties of starch melt has a strong influence on the
24 macroscopic expansion behaviour [168]. Vergnes et al. [101] found that cross-
25 sectional expansion index (SEI, calculated as the cross-sectional area of the extrudate

1 divided by the cross-sectional area of the die) of starch polymer melt could be varied
2 by shear rate at the die when the same thermomechanical treatment was imposed. The
3 higher the shear rate, the larger the SEI was observed. This is related to the shear-
4 thinning behaviour of starch polymer melt. A lower viscosity at higher shear rate
5 made the expansion easier, which is in agreement with the bubble growth theory [169].
6 Ilo et al. [110] discovered that melt viscosity, along with moisture content, had a
7 significant influence on the SEI. The SEI decreased with increasing melt viscosity at
8 higher moisture content, which is in line with bubble growth theory [169]. However,
9 the SEI increased with increasing melt viscosity at low moisture content, which may
10 due to the higher stored energy of starch molecules during their flow through the die
11 at higher melt viscosity [170]. Della Valle et al. [128] found that, for the TPS samples
12 with different amylose contents, volumetric expansion index (VEI, defined by the
13 ratio of the corresponding specific dimension of the extrudate to that within the die,
14 multiplied by moisture correction factor) increased as melt viscosity decreased at
15 given moisture content and temperature. However, it was claimed that higher
16 moisture content, which reduced the viscosity as well, might result in a drop of VEI
17 [128], which cannot be explained by simple bubble growth.

18 Fan et al. [171] developed a model to describe the dynamics of bubble growth and
19 shrinkage in starchy extrudate: a bubble cell first grows by rapid vaporisation of the
20 superheated moisture, and subsequently shrinks by the cooling of vapour which
21 produces a negative pressure difference. The power-law model (cf. Eq. 3 and 4) is
22 used to calculate the shear viscosity of the extrudate in the former stage of bubble
23 growth, with the shear rate of the expanding bubble taken as:

$$24 \quad \dot{\gamma} = \frac{\dot{R}}{2R} \quad (20)$$

25 where R is the bubble radius and \dot{R} is the rate of change in R . In the latter stage of

1 growth, the temperature of the melt will approach the T_g (i.e. $T \leq T_g + 50$), and the
 2 shear rate will be very small; hence, the η_0 calculated from Williams-Landel-Ferry
 3 (WLF) equations is used to describe the shear viscosity of the extruded melt:

$$4 \quad \log \frac{\eta_0}{\eta_{T_g}} = \frac{-17.44 \times (T - T_g)}{51.6 + (T - T_g)} \quad (21)$$

5 where η_{T_g} is the shear viscosity at the T_g , taken equal to 10^{14} Pa·s [172], and the T_g is
 6 taken from a modified Couchman-Karasz equation [173]. With the viscosity value of
 7 the melt, the model for the bubble dynamics can be expressed as:

$$8 \quad P_b - P_a = \frac{2\sigma}{R} + 4\eta_a \frac{\dot{R}}{R} \quad (22)$$

9 where P_a is the vapour pressure inside a bubble; P_a is the ambient pressure; and σ is
 10 the surface tension. Fan et al. [171] found that melt viscosity is the dominant factor
 11 resisting cell growth and shrinkage, whereas surface tension has negligible effect. It
 12 was also shown that the activation energy, E/R (cf. Eq. 4) had a very strong effect. A
 13 decrease of E/R value, which means lowering the viscosity, gave rise to faster
 14 expansion of a bubble just before its severe collapse; higher viscosity as a result of
 15 higher E/R value delayed the growth, but slight shrinkage was observed because the
 16 low maximum bubble radius obtained reduces the heat and mass transfer area
 17 resulting in a slower drop in temperature and moisture and hence a smaller increase in
 18 viscosity. The change in α (cf. Eq. 4) exerted a profound impact on the expanding
 19 rate but appears to have similar final bubble sizes. A rise in n (cf. Eq. 3) retarded the
 20 growth but enhanced the shrinkage. The model by Fan et al. [171], however, didn't
 21 take into account the effects of limitations imposed by the diffusion of water, and
 22 bubble coalescence and rupture. A more compressive dynamics model was later

1 developed by Alavi et al. [174,175] for sc-CO₂ extrusion and post-extrusion
2 processing of starchy extrudates.

3 By X-ray tomography study of the cell structure of extruded starches, Babin et al.
4 [176] discovered that a decrease of shear viscosity resulting from an increase of shear
5 rate can increase the mean cell size but decrease the cell number density (N_c). This
6 was explained by an increase of coalescence as suggested by Park et al. [177].

7 Besides, the reduced nucleation activity was attributed to the higher gas diffusivity
8 and lower pressure drop rate in a less viscous melt [178-180]. Indeed, for faster
9 bubble growth, the resulting decrease of resistance of the melt to extensional flow
10 favours wall rupture. Babin et al. [176] also reported that samples containing less
11 amylose were less expanded. It was explained that lower extensional viscosity results
12 from lower amylose content, and lower resistance of the melt to extensional flow
13 favours coalescence within these materials, upon cooling in the vicinity of T_g , just
14 before foam setting, leading to a larger density. In summary, at larger temperature,
15 the bubble growth is favoured by low viscosity, as reflected by the influence of shear
16 viscosity; but, for lower temperature closer to T_g and foaming setting, lower values of
17 extensional viscosity would finally contribute to reduce the void volume [176]. This
18 theory can also explain the results in a number of other studies [124,143,161].

19

20 6.3. *Rheology-film blowing property relationship*

21 Generally, a high extensional viscosity is favourable for film blowing since it
22 increases take-up force which enhances bubble stability. It has been established that
23 higher extensional viscosity can be obtained by the increase of molecular weight and
24 the generation of strain hardening [165]. In addition, strain hardening is also

1 favourable for the homogeneity of film thickness [165]. This is also true for starch
2 polymers as reported by Zullo and Iannace [160].

3 Thunwall et al. [96] investigated the relationships between the processing
4 parameters (glycerol content, moisture content, and temperature) that influence the
5 shear viscosity and the film blowing properties of TPS. It has been showed that, when
6 the shear viscosity is higher than a critical value, TPS become too stiff to expand
7 during the blowing and the material fails in a brittle manner at the calendering nip.
8 Moreover, the significant increase in the torque required from the extruder and the die
9 pressure as a result of high viscosity also makes the film blowing process difficult
10 [96]. In contrast, when the viscosity is too low, the surface of the extruded material
11 become sticky, resulting in a double-walled film impossible to separate through the
12 calendering nip. A low viscosity accompanied by high temperature and high
13 plasticiser content might also cause the bubble formation in the extrudate, and the
14 subsequent rupture of the stretched melt [96]. These relationships are illustrated in
15 [Fig. 13](#).

16

17 [Insert [Fig. 13](#) here]

18

19 *6.4. Other rheology-processing/product property relationships*

20 In extrusion processing, a higher viscosity may result in enhanced
21 thermomechanical treatment ($SME = \Gamma \times N/Q$) within the extruder barrel, which may
22 cause a greater degree of molecular degradation which could deteriorate the
23 mechanical properties of final products [58,84,108,113,127,130]. In injection
24 moulding with a given back-pressure, a lower melt viscosity can result in a higher
25 backward flow rate and thus a longer refill time (a lower net flow rate) [181]; besides,

1 the adhesion of TPS part to the mould can occur at low viscosity (though the adhesion
2 can be minimised by using an appropriate lubricant) [45]. In various kinds of
3 processing, viscosity can affect the mechanical properties since it has a relationship
4 with blend compatibility and morphology as already discussed in [Section 6.1](#).
5 Furthermore, it can be expected that an appropriate viscosity is important for the
6 orientation process of TPS products which would improve the mechanical properties
7 [144,182].

8

9 **7. Summary**

10 Various rheometric techniques have been employed to understand the processing
11 rheology of starch polymeric materials. Among them, those having strong
12 thermomechanical input and the abilities to prevent the moisture loss and to handle
13 the high viscosity of starch polymeric materials are preferable. An off-line extruder-
14 type capillary/slit rheometer is a popular choice due to its high efficiency for a series
15 of samples; however, subsequent changes during the measurement run are often
16 unavoidable. When an in-line method is used, the choice of a DCD is recommended,
17 of which the extra flow channel can effectively adjust the shear rate while minimise
18 the change in processing history at different testing conditions. In addition, a pre-
19 shearing rheometer is a useful tool to understand the rheological properties of
20 accurately melted products. Moreover, MPR is also a valuable tool due to its many
21 advantages that has already been demonstrated in the studies of many other polymers
22 and fluids [183]. Nevertheless, the use of MPR in the rheological studies of starch
23 polymers has just been started.

24 The rheological properties of starch polymers can be impacted by their
25 formulation (plasticiser, additive, starch structure, (nano)filler, other (bio)polymer,

1 etc.) and processing conditions (SME, temperature, etc.). Starch polymer melts
2 exhibit shear-thinning and extension-thinning behaviours, and shows strong elastic
3 properties. The viscous heat dissipation as affected by processing rheology should
4 never be ignored especially for starch polymers with a relatively high viscosity.
5 Different rheological models have been proposed based on different systems. A well
6 understanding of the processing rheology of starch polymers can help us not only
7 determining optimal processing method and conditions, but also better controlling the
8 quality of the products by linking rheology to various physical properties.

9

10 **8. Future perspectives**

11 In spite of the progress in the rheology of starch polymers, some problems still
12 exist and much work needs to be done in the future. In addition, new development in
13 starch polymers and their processing techniques also requires our continuous efforts.
14 Here, two perspectives are proposed as references for people with the same interest:

15 1) Viscoelastic properties and extensional viscosity

16 As discussed in [Section 5.2](#), during processing, shear viscosity may not be
17 sufficient to characterise the rheology of starch polymers. Starch polymer melts can
18 display strong melt elastic properties, which relates to the processing and product
19 quality. Also many processing flows are mixed flow – both shear and extensional
20 flows – and thus extensional viscosity measurements are also vital. New techniques
21 need to be developed for the more accurate characterisation of the elasticity of starch
22 polymer melts. Much work needs to be done to establish the relationships between
23 formulation and processing conditions, and melt viscoelastic properties and
24 extensional viscosity. It is also worth to carry out research to link the melt elastic
25 properties to product properties of starch polymers. Regarding this, strain hardening

1 behaviour which can be related to processes such as foaming and film blowing should
2 be a focus.

3 2) “Complete” modelling

4 The changes in starch under processing are not only affected by temperature,
5 plasticiser, and SME, but also are affected by thermal energy input and pressure.
6 Additionally, there is currently no simple relationship between starch granular
7 transformation and macromolecular degradation, and melt viscosity. It has been
8 shown that, under thermomechanical treatment, the viscosity of starch with low
9 content of plasticiser first increases and then decreases to a nearly stable value [31,32].

10 As a result, the processing-structure-rheology relationship needs to be carefully
11 examined. Furthermore, it is meaningful to differentiate the effects of temperature
12 and plasticiser on starch microstructural changes (which subsequently impact the
13 rheology) from those affects directly on the rheology.

14 Different parameters (temperature, plasticiser content, SME, etc.) in current
15 empirical models actually interacts with each other, which has to be considered into
16 future modelling work. More importantly, the rheology of starch as a polymer
17 depends on not only temperature and plasticiser content, but also structural factors
18 such as molecular weight, polydispersity, conformation, and composition.
19 Rheological modelling should consider these structural factors and based on structural
20 models (e.g. the hard sphere suspension model), enabling the linkage between
21 rheology and polymer physics and chemistry. In this way we are moving toward the
22 development of a “complete” constitutive rheological model for starch polymeric
23 materials.

24

25

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Figure captions

- Fig. 1 The role of rheology in starch polymer processing (black colour stands for the traditional focuses while blue colour illustrates the emphases in this paper). The solid line means “influences” and the dash line means “gives information about”.
- Fig. 2 Schematic representation of starch processing by extrusion
- Fig. 3 Schematic representation of the Rheoplast. 1, Hopper; 2, annular piston; 3, inner piston; 4, barrel; 5, shearing chamber; 6, injection pot; 7, pressure transducer; 8, capillary; 9, thermocouple. Reprinted from [101], Copyright (1987), with permission from Elsevier.
- Fig. 4 Schematic diagram of the extruder with a side-stream valve and the slit die rheometer. The slit height $H = 0.12$ cm and the slit width $W = 1.79$ cm. Reprinted from [119], Copyright (1993), with permission from Elsevier.
- Fig. 5 Schematic view of the Rheopac system. Reprinted from [128], Copyright (1997), with permission from Elsevier.
- Fig. 6 Bifurcated flow, dual orifice die. Reprinted from [131], Copyright (2002), with permission from Elsevier.
- Fig. 7 Schematic 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. Reprinted from [135], Copyright (2011), with permission from Elsevier.
- Fig. 8 Consistency values of wheat starch polymer melt versus the SME. The filled circles represent the data obtained under different test conditions (temperature:

110–150 °C; moisture content: 10–20%, wet basis; glycerol content: 10–35%, wet basis), whereas the open circles were obtained after a temperature correction from the same experimental data set. Reprinted from [84], Copyright (2003), with permission from Elsevier.

Fig. 9 Rheological mastercurves of waxy starch polymer melt at $T_0 = 110$ °C, $GC_0 = 54\%$, and $MC_0 = 36\%$, obtained by time–temperature–moisture content–glycerol content superposition (plotting $\eta/a_{T \cdot MC \cdot GC}$ as a function of $\gamma \cdot a_{T \cdot MC \cdot GC}$ where $a_{T \cdot MC \cdot GC}$ is the shift factor defined as:

$$a_{T \cdot MC \cdot GC} = \exp \left[\frac{E}{R} \left(\frac{1}{T_i} - \frac{1}{T_0} \right) - \alpha(GC_i - GC_0) - \alpha'(MC_i - MC_0) \right]$$

of the results measured at various T_i , GC_i , and MC_i conditions. Reprinted from [135], Copyright (2011), with permission from Elsevier.

Fig. 10 Schematic representation of microstructural changes in starch under processing with different plasticisers. Reprinted from [135], Copyright (2011), with permission from Elsevier.

Fig. 11 Rheological mastercurves of amylo maize starch (amylose content = 70%, A) and waxy maize starch (amylose content = 0%, D) at $T_0 = 165$ °C and $MC_0 = 0.245$, obtained by time–temperature–moisture superposition (cf. the caption of Fig. 12). (A: intrinsic viscosity 93 ml/g; B: intrinsic viscosity 81 ml/g). Reprinted from [127], Copyright (1996), with permission from the Journal of Rheology (The Society of Rheology, Inc.) and the author Guy Della Valle.

Fig. 12 Viscosity ratios of TPS to PHEE vs. shear rates (moisture content on wet basis). Reprinted from [55], Copyright (2000), with permission from Elsevier.

Fig. 13 Illustration of the limiting processing parameters (temperature, MC, and GC) in film blowing of TPS. Two counteracting factor towards film forming are

bubble formation in the extrudate which subsequently results in the rupture of the stretched melt, and high shear viscosity which lowers the melt tenacity for satisfactory expansion. Reprinted from [96], Copyright (2008), with permission from Elsevier.

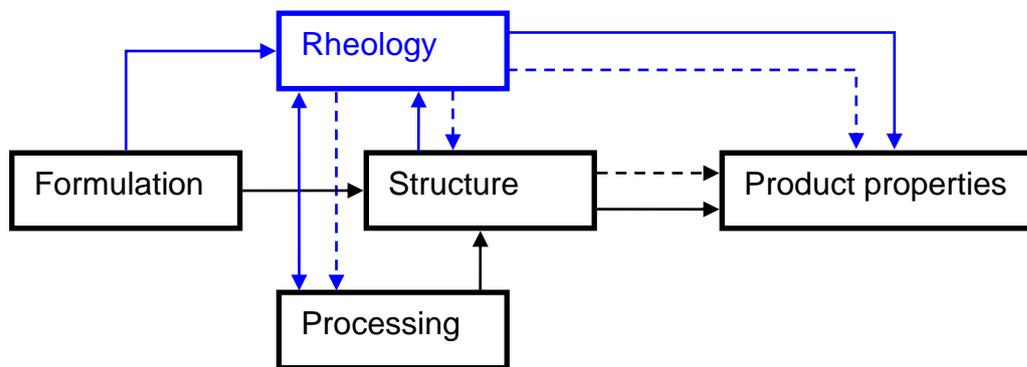


Fig. 1 – Xie et al.

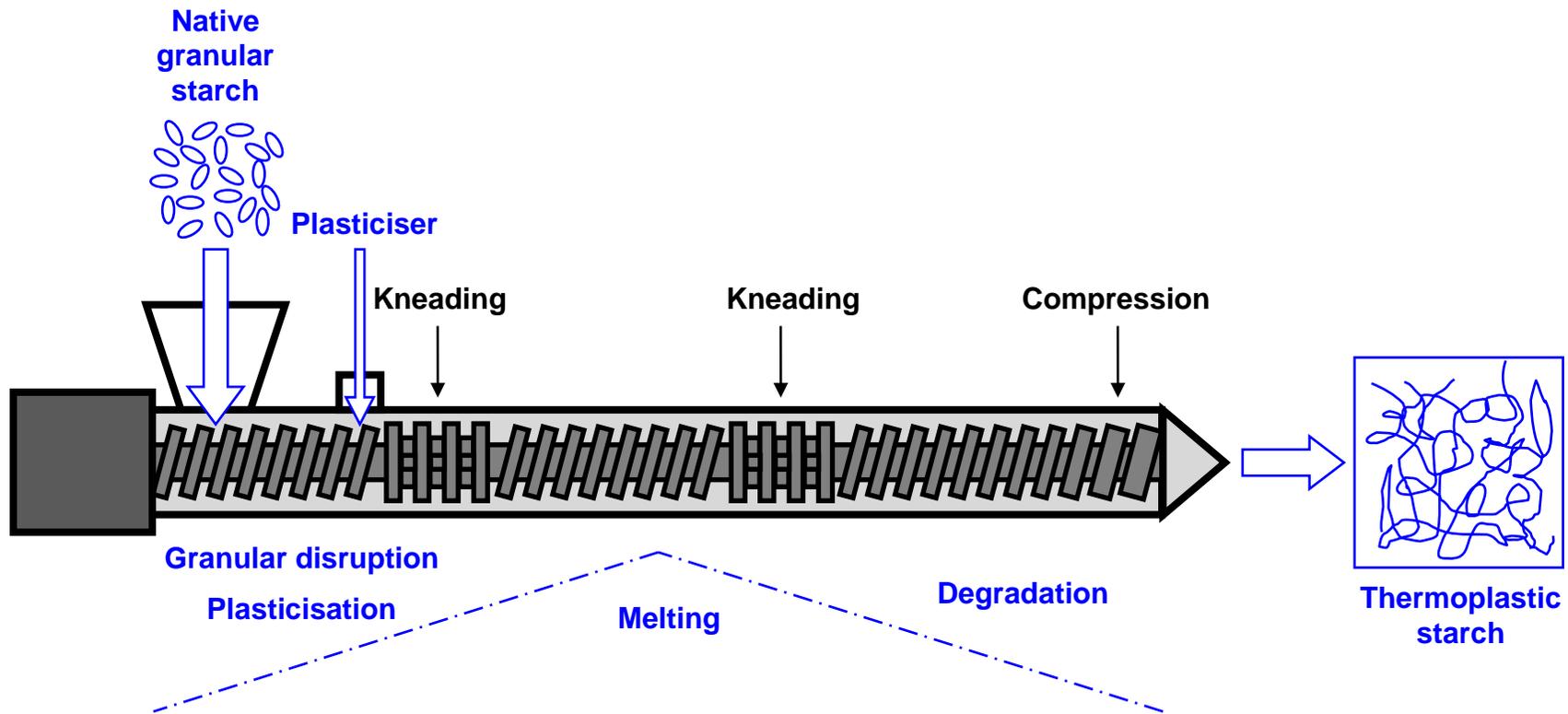


Fig. 2 – Xie et al.

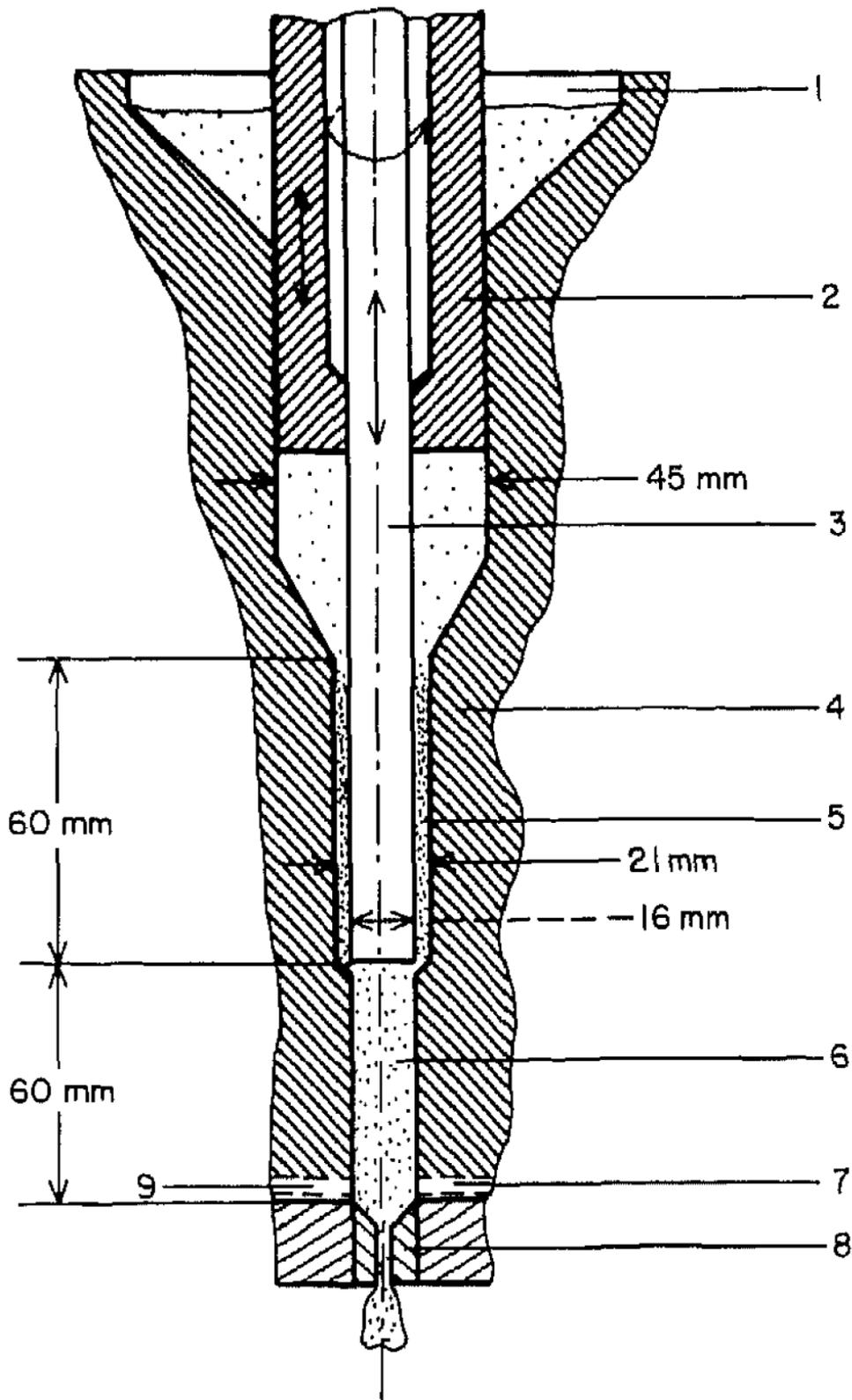


Fig. 3 – Xie et al.

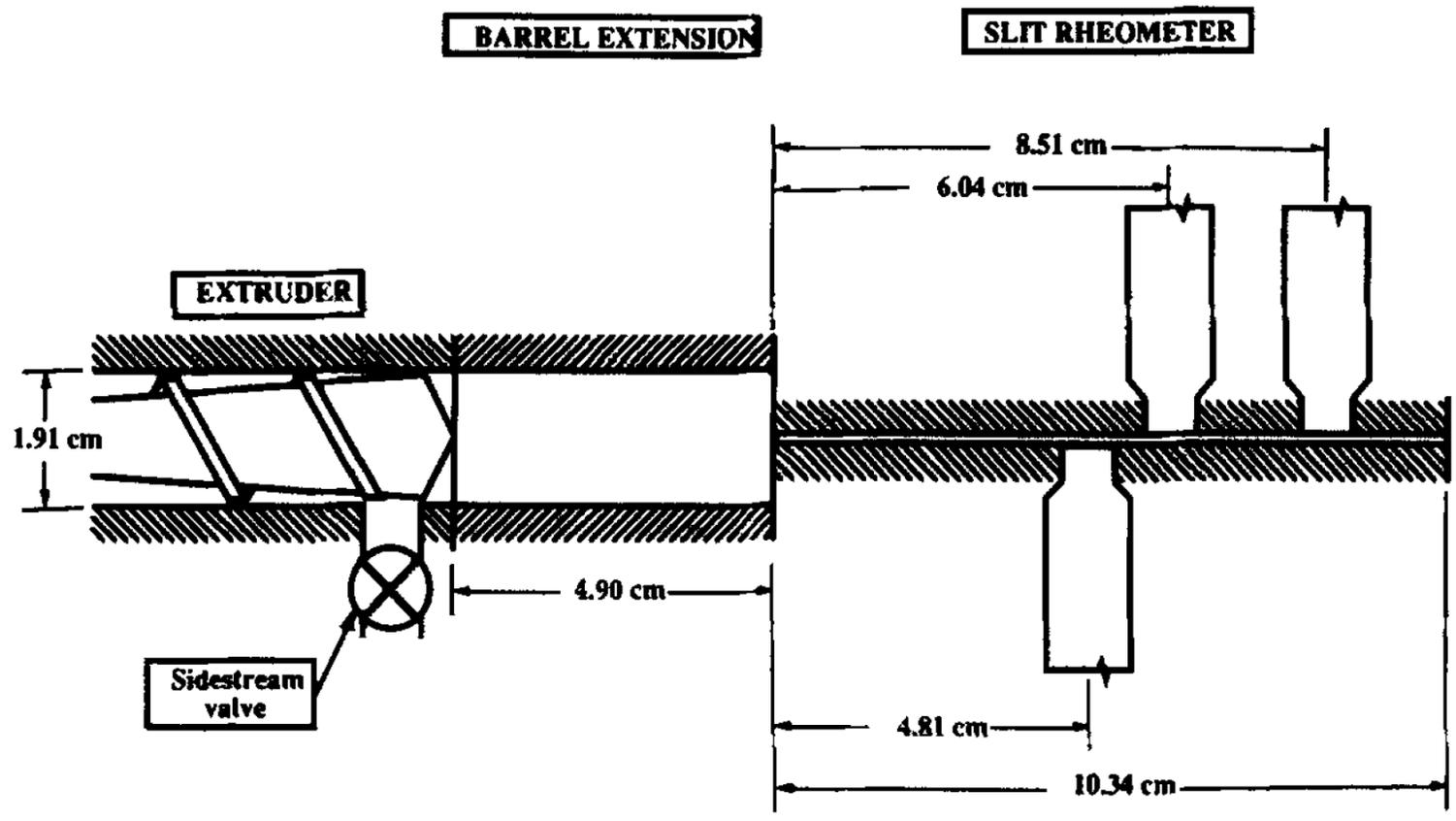


Fig. 4 – Xie et al.

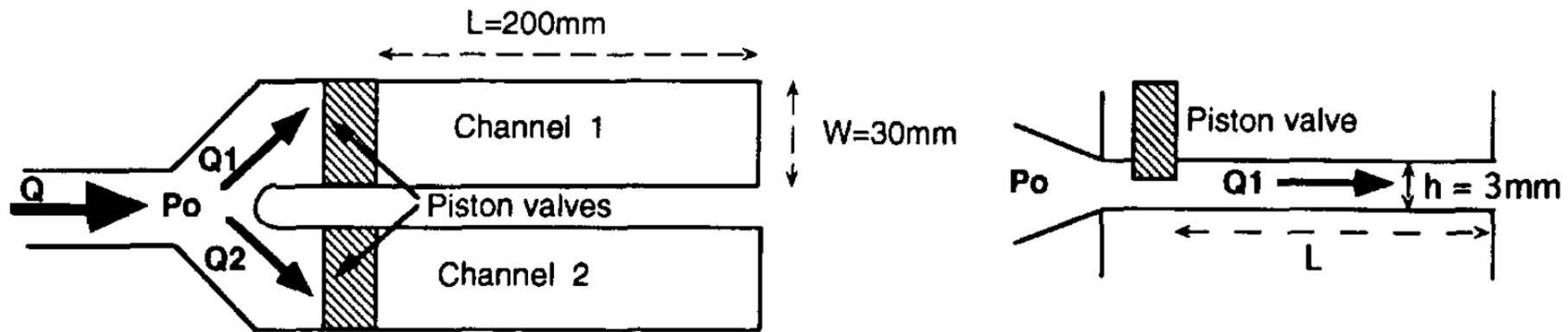


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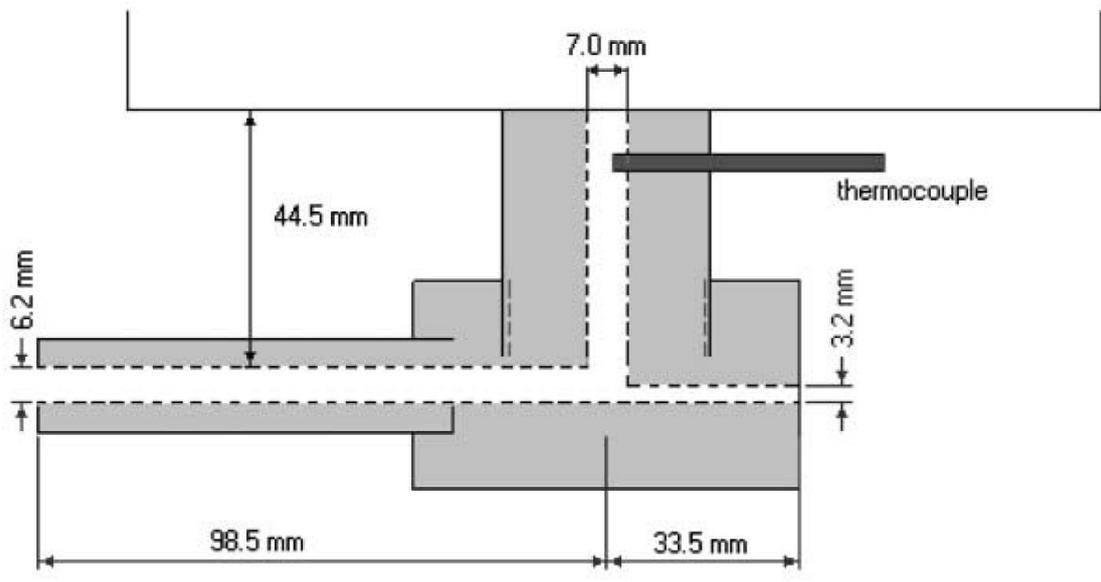


Fig. 6 – Xie et al.

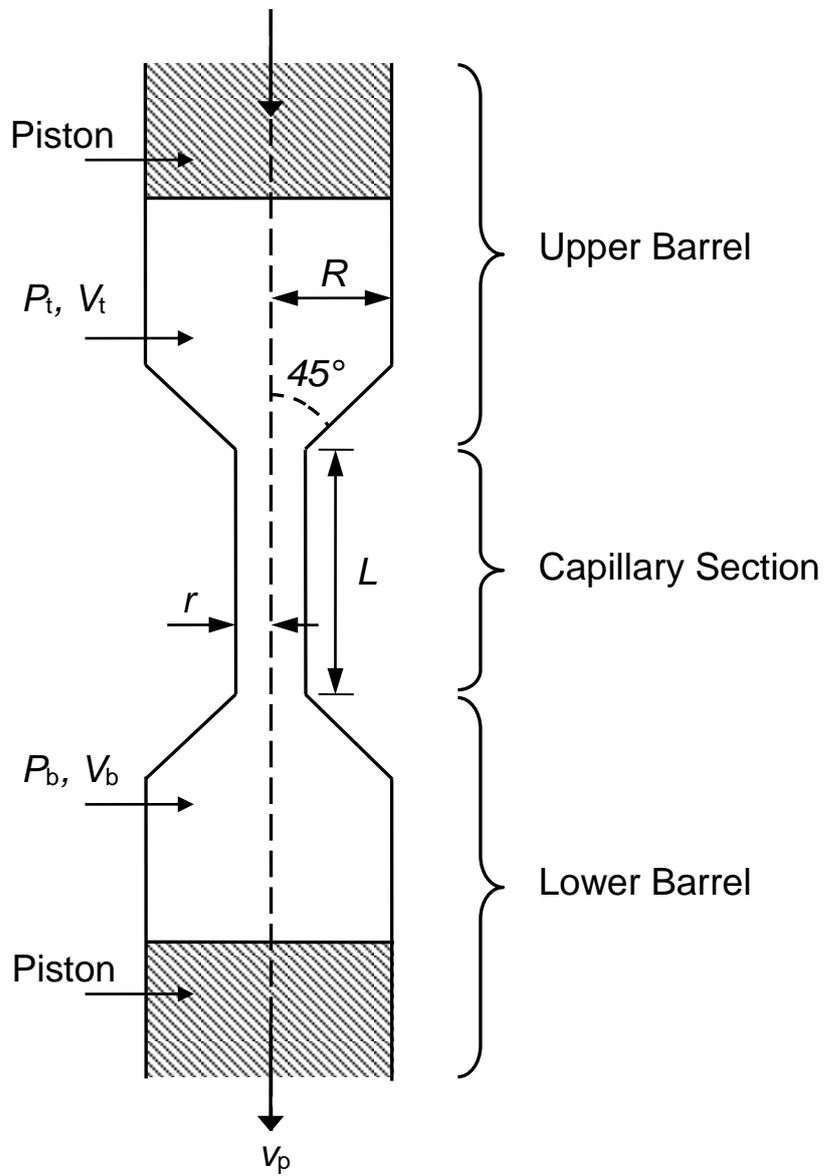


Fig. 7 – Xie et al.

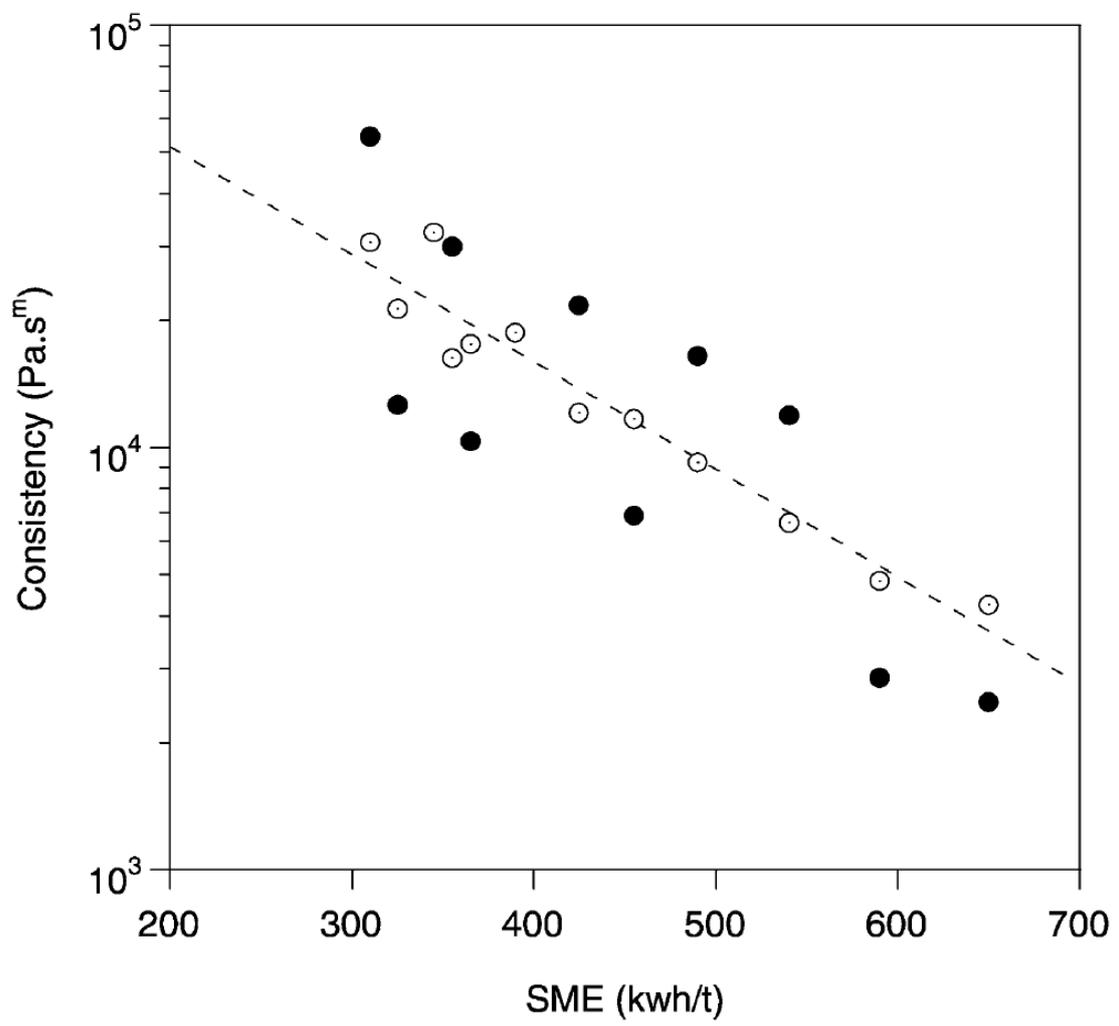


Fig. 8 – Xie et al.

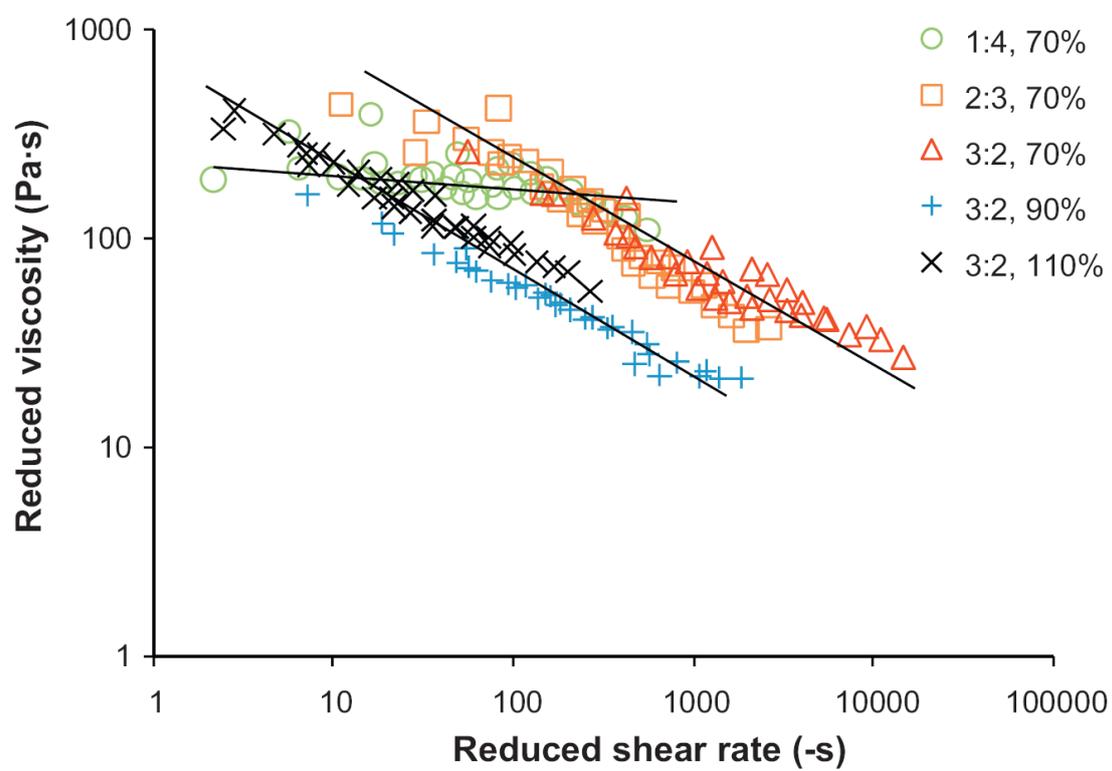


Fig. 9 – Xie et al.

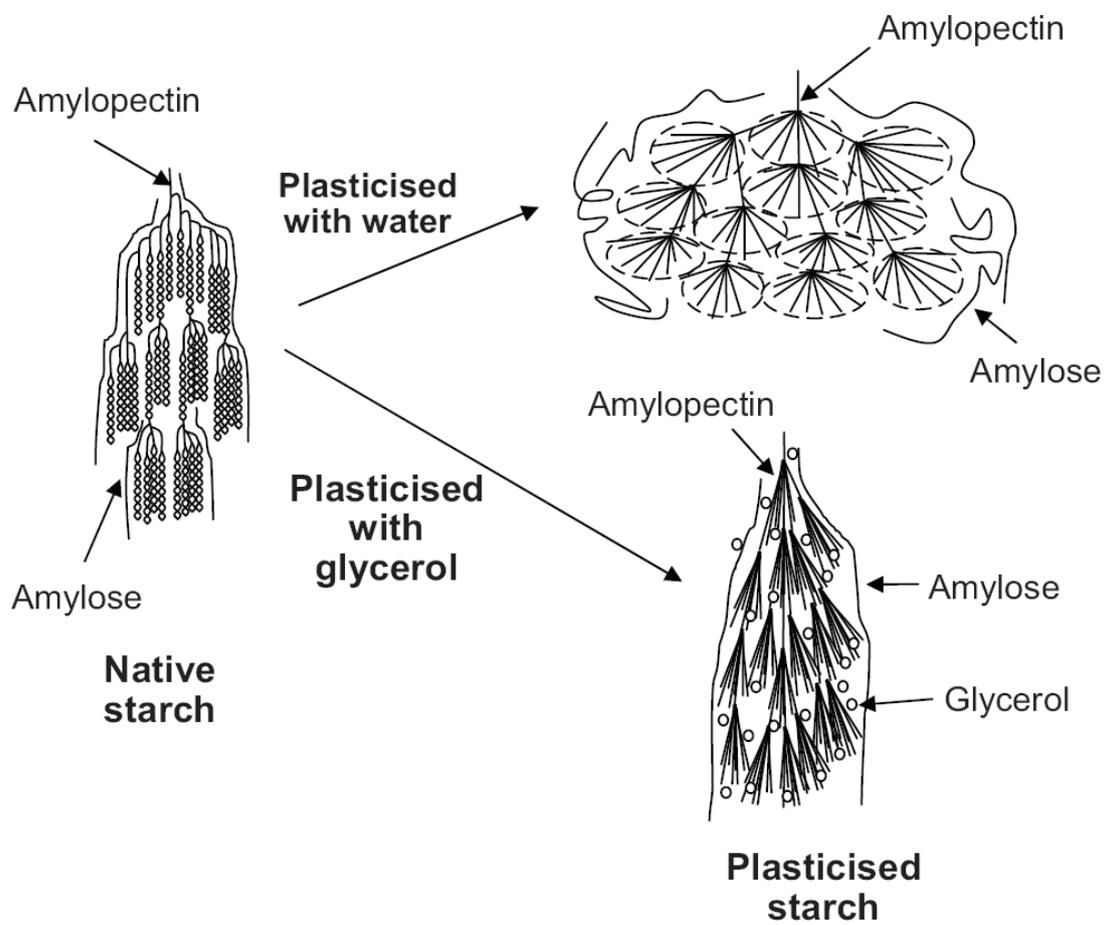


Fig. 10 – Xie et al.

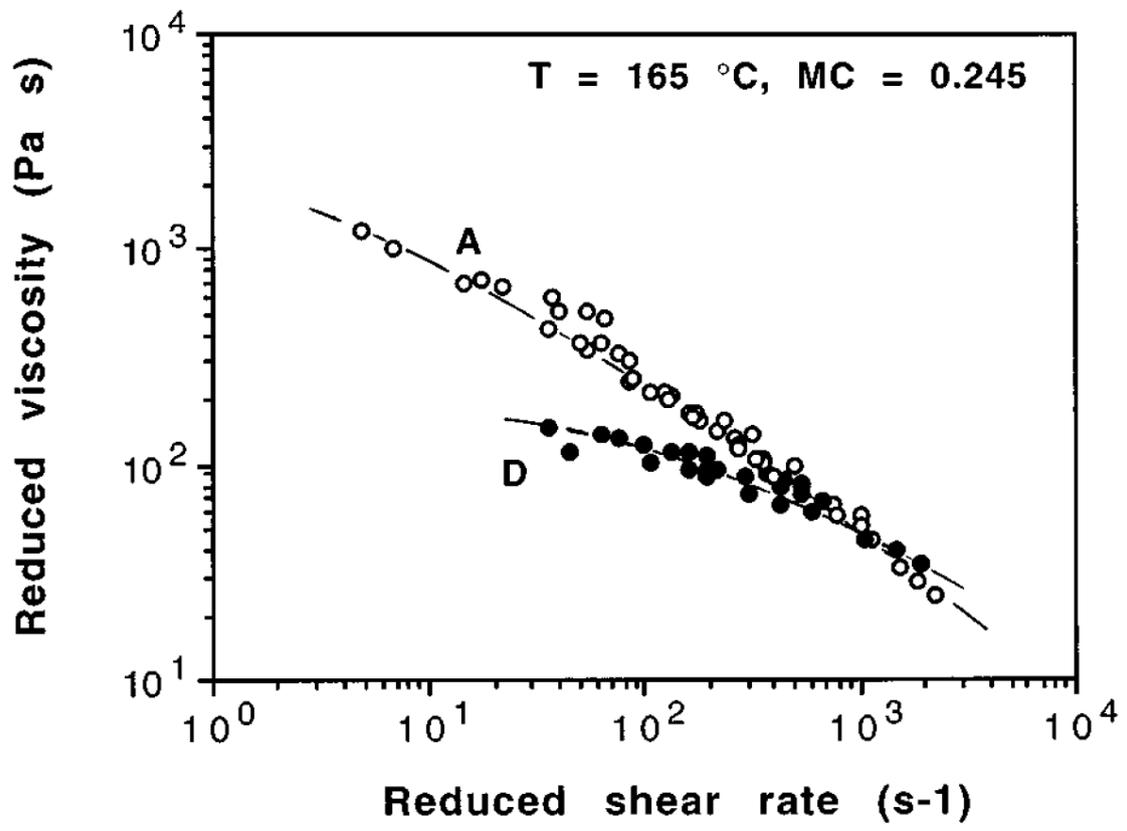


Fig. 11 – Xie et al.

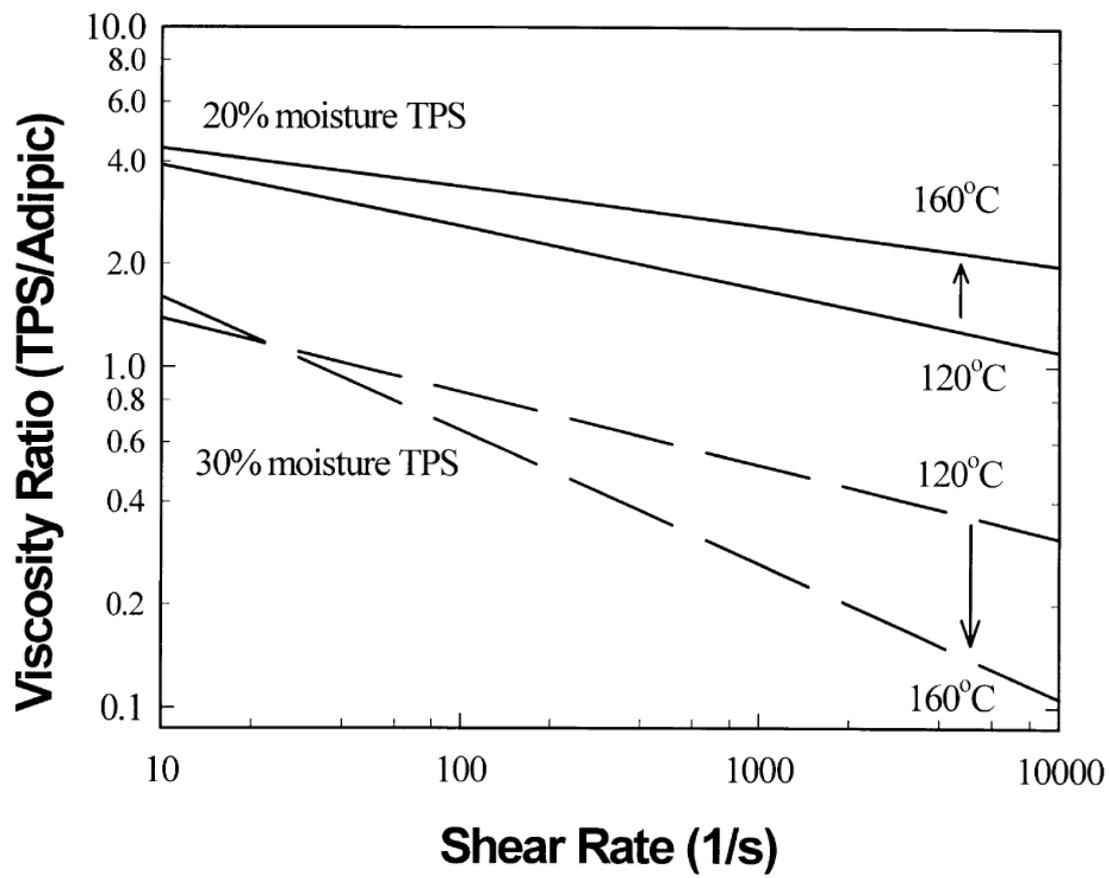


Fig. 12 – Xie et al.

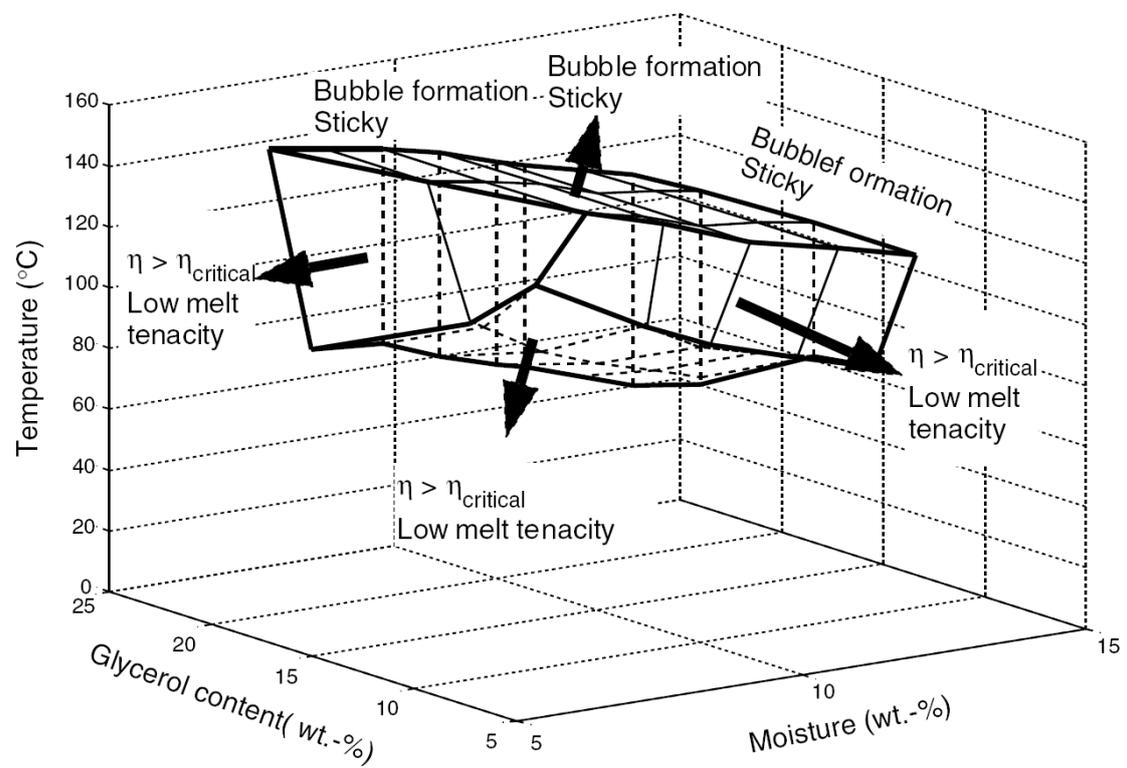


Fig. 13 – Xie et al.

Tables

Tab. 1 The relative proportions of amorphous, single, and double-helix conformations for starches of varying amylose content along with their X-ray diffraction (XRD) patterns and degree of crystallinity. Adapted with permission from [17]. Copyright 2007 American Chemical Society.

Starch	Amylose content ^a (%)	Relative proportion ^b (%)			Degree of crystallinity ^c	XRD pattern
		V-type polymorph	Double-helix	Amorphous		
Waxy maize	3.4	0	47	53	29	A
Regular maize	24.4	3	33	64	21	A
Amylomaize (Gelose 50)	56.3	7	18	75	13	B
Amylomaize (Gelose 80)	82.9	14	38	68	15	B

^aThe maximum error for amylose content determination was 6%. ^bThe maximum standard deviation for the ¹³C NMR analysis calculation was 2.4%. ^cThe maximum error for the calculation of degree of crystallinity was 3.5%.

Tab. 2 Comparison of the different rheometric systems for starch polymer melts

Type	Rheometer	Shear rate variation method	Measurement type ^a	Advantage	Disadvantage	Shear rate (s ⁻¹) / frequency (rad/s) ^a	Reference
Off-line	Rotational	Rotation speed	Viscoelasticity	Small amount of sample	Serious loss of water; insufficient SME input for melting starch	10 ⁻² –10 ²	[88]
	Plunger-type slit/capillary	Plunger moving speed	Steady shear viscosity; extensional viscosity; first normal stress difference	Small amount of sample; easy to use; for pre-shearing rheometer (Rheoplast), the processing conditions are independently controlled.	Insufficient SME input for melting starch; minor loss of water and unstable results (pre-shearing rheometer)	10 ⁻¹ –10 ⁵	[45, 47, 51, 83, 93, 94, 97, 99, 100, 101, 103, 160, 162]
	Extruder-type slit/capillary	Screw speed	Steady shear viscosity; extensional viscosity; first normal stress difference	Multi-step extrusion processing and post processing conditioning allowed	Subsequent degradation	10 ¹ –10 ³	[52, 54, 65, 105, 107, 108]

In-line	SSE +	Screw speed	Steady shear viscosity;	Approximate the practical	Change in	10^0 – 10^4	[2, 48, 53, 84, 113]
	CDV/SDV		extensional viscosity;	extrusion process	thermomechanical history		
			first normal stress difference				
In-line	TSE +	Feeding rate	Steady shear viscosity;	Approximate the practical	Change in	10^1 – 10^3	[93, 110, 112, 117]
	CDV/SDV			extrusion process	thermomechanical history		
In-line	SSE/TSE +	Die channel flow restrictions	Steady shear viscosity;	Approximate the practical	–	10^0 – 10^3	[77, 78, 85, 119, 120, 130, 131]
	DCD		extensional viscosity;	extrusion process; no/little			
			first normal stress difference	change in thermomechanical history			
Other	Multipass	Piston moving speed	Steady shear viscosity	Small amount of sample; no loss of water	Steady rheological state is required.	10^1 – 10^3	[135]
	Mixer-type	Rotor speed	Steady shear viscosity,	Small amount of sample	Minor loss of water; shear stress and shear rate are approximately calculated; steady rheological state is required.	10^1 – 10^3	[137]

SSE: single-screw extruder; TSE: twin-screw extruder; CDV: capillary/cylindrical die viscometer; SDV: slit die viscometer; DCD: double-channel die.

^a According to the published results in the literature

Tab. 3 Summary of the different shear viscosity power-law models used in the literature

Reference	Sample	Experimental set-up	Temp. (°C)	Plasticiser content (%)	Other remarks	Shear rate (s ⁻¹)	Rheological model (K)	Constants
Harper et al., 1971 [140]	Cereal dough (80% maize and 20% oat flour)	Off-line (SSE+CDV)	67–100	MC: 25–35 (w.b.)	The dough was prepared in a continuous agitated cooker	10 ¹ –10 ²	$K = K_0 \exp(E/RT - \alpha MC)$	$E/R = 2482; \alpha = 0.079; K_0 = 78.5; n = 0.51$
Cervone and Harper, 1978 [118]	Maize flour (pregelatinised)	In-line (SSE+SDV)	90–150	MC: 22–30 (d.b.)	–	10 ¹ –10 ²	$K = K_0 \exp(E/RT - \alpha MC)$	$E/R = 4388; \alpha = 0.101; K_0 = 36.0; n = 0.36$
Fletcher et al., 1985 [139]	Maize girts	In-line (SSE+SDV)	153–158	MC: 15–19 (d.b.)	–	10 ¹ –10 ³	$K = K_0 \exp(E/RT - \alpha MC)$	$E/R = 3969; \alpha = 0.03; K_0 = 0.49; n = 0.68$

Vergnes and Villemaire, 1987 [100]	Maize starch	Pre-shearing	110–170	MC: 21–33 (w.b.)	–	10^1 – 10^3	$K = K_0 \exp[E/R(1/T - 1/T_0) - \alpha(MC - MC_0) - \beta(W - W_0)]$ $n = \alpha_1 T + \alpha_2 MC + \alpha_{12} T \cdot MC$	$\Delta E/RT = 4250$; $\alpha = 10.6$; $\beta = 0.088$; $K_0 = 7.36$; $\alpha_1 = 6.59 \times 10^{-4}$; $\alpha_2 = 1.12 \times 10^{-1}$; $\alpha_{12} = 7.28 \times 10^{-3}$
Senouci and Smith, 1988 [93]	Maize grits	In-line (TSE+SDV) Off-line (PCR)	100–140	MC: 20.1– 31.5 (w.b.)	–	10^1 – 10^3	$K = K_0 N^{-k} \exp(E/RT - \alpha MC)$	$E/R = 2834$; $\alpha = 0.032$; $k = 0.541$; $K_0 = 21.5$; $n = 0.75$
Lai and Kokini, 1990 [113]	Waxy maize starch	In-line (SSE+CDV/S DV)	100–150	MC: 20–40 (w.b.)	The use of both CDV and SDV ensured a wide shear rate range.	10^0 – 10^3	$K = K_0 \exp[(E + E' MC)/RT - (\alpha + \alpha' T) MC] (DG)^k$	$E/R = 50168$; $E'/R = -3159$; $\alpha = 11.502$; $\alpha' = -0.0093$; $k = 0.056$; $K_0 = -112.45$; $n = 0.312$
Wang et al., 1990 [117]	Wheat flour	In-line (TSE+CDV)	169–187	MC: 18–24 (w.b.)	The use of three viscometer geometries ensured a wide shear rate range.	10^1 – 10^3	$K = K_0 \exp[-\alpha MC] (1 - \beta W)$	$\alpha = 8.71$; $\beta = 9.8 \times 10^{-4}$; $K_0 = 3.62 \times 10^{-5}$; $n = 0.15$

Padmanabhan and Bhattacharya, 1991 [114]	Maize meal	In-line (SSE+SDV)	150–180	MC: 25–45 (d.b.)	–	10^2 – 10^3	$K = K_0 \exp(E/RT - \alpha MC + kP_b)$	$E/R = 2726 \text{ K}; \alpha = 1.99; k = 3.5 \times 10^{-8}; K_0 = 249; n = 0.28$
Padmanabhan and Bhattacharya 1993 [119]	Maize meal	In-line (SSE+DCD)	160–180	MC: 25–35 (d.b.)	–	10^1 – 10^3	$K = K_0 \exp(E/RT - \alpha MC)$	$E/R = 2451; \alpha = 4.63; K_0 = 106.25; n = 0.37$
Della Valle et al., 1995 [58]	Potato starch	In-line (TSE+Rheopa c)	139–176	MC: 26–32 (w.b.)	–	10^1 – 10^3	$K = K_0 \exp[E/R(1/T - 1/T_0) - \alpha(MC - MC_0) - \beta(SME - SME_0)]$ $n = n_0 + \alpha_1 T + \alpha_2 MC + \alpha_3 SME$ $\alpha_{12} T \cdot MC + \alpha_{13} T \cdot SME + \alpha_{23} MC \cdot SME$	$\Delta E/RT = 5710; \alpha = 9.45; \beta = 1.56 \times 10^{-9}; K_0 = 0.34; \alpha_1 = 0.997; \alpha_2 = -60.6; \alpha_3 = 0.044; \alpha_{12} = 0.418; \alpha_{13} = 2.1 \times 10^{-4}; \alpha_{23} = -0.0341; \alpha_{13} = -2.1 \times 10^{-4}; n_0 = 14.33$
Wang et al., 1995 [57]	Maize starch-PVA blends (3/1, w/w)	Offline (PCR)	100–120	MC: 26–45 (w.b.)	–	10^1 – 10^4	$K = K_0 \exp(E/RT - \alpha MC)$	$E/R = 6332.5; \alpha = 6.1; K_0 = 1.391 \times 10^{-2}; n = 0.31$

Willet et al., 1995 [108]	Maize starch	Offline (SSE+CDV)	110–180	MC: 15–30	–	10^1 – 10^3	$K = K_0 \exp(E/RT - \alpha MC)$	$E/RT = 8500$; $\alpha = 12.6$; K_0 and n not determined.
Della Valle et al., 1996 [127]	Maize starch (23% amylose content)	In-line (TSE+Rheopa c)	130–160	MC: 20.5– 36.0 (w.b.)	–	10^1 – 10^3	$K = K_0 \exp(E/RT - \alpha MC - \beta SME)$ $n = n_0 + \alpha_1 T + \alpha_2 MC + \alpha_3 SME$ $+ \alpha_{12} T \cdot MC + \alpha_{13} T \cdot SME + \alpha_{23} MC \cdot SME$	$E/R = 6140$; $\alpha = 18.6$; $\beta = 2.1 \times 10^{-3}$; $K_0 = 0.163$; $\alpha_1 = -1.54 \times 10^{-2}$; $\alpha_2 = -3.19$; $\alpha_3 = -3.14 \times 10^{-2}$; $\alpha_{12} = \text{ns}$; $\alpha_{13} = 1.473 \times 10^{-4}$; $\alpha_{23} = 4.06 \times 10^{-2}$; $n_0 = 3.54$
Ilo et al., 1996 [110]	Maize grits	In-line (TSE+CDV)	150–160	MC: 13–17 (w.b.)	–	(Not given)	$K = K_0 \exp(E/RT - \alpha MC)$	$E/R = 18441$; $\alpha = 0.097$; $K_0 = 7041$; $n = 0.15$
Aichholzer and Fritz, 1998 [106]	(Starch type not given)	Off-line (SSE+piston+ SDV)	70–110	MC: 12.5 GC: 15–25	Sample ageing and screw shear during measurement had no significant effect.	10^0 – 10^4	$K = K_0 \exp\{1/R[(g_1 + g_2 GC)(1/T_0 - 1/T) + (t_1 + t_2 T)(1/GC_0 - 1/GC)]\}$	$g_1 = -1.47 \times 10^3$; $g_2 = 1.62 \times 10^5$; $t_1 = 6.45 \times 10^5$; $t_2 = -1.20 \times 10^3$; K_0 and n not determined.

Brouillet- Fourmann et al., 2002 [137]	Maize flour	Mixer	89–115	MC: 25–30 (w.b.)	Steady molecular and rheological state was achieved before measurements.	10^2 – 10^3	$K = K_0 \exp(E/RT - \alpha MC)$	$E/R = 3090$; $\alpha = 10.64$; $K_0 =$ 566 ; $n = 0.23$
Martin, et al., 2003 [84]	Wheat starch	In-line (SSE+CDV; SSE+SDV)	110–150	MC: 0–20 (w.b.) GC: 10–35 (w.b.)	The use of both CDV and SDV ensured a wide shear rate range.	10^1 – 10^4	$K = K_0 \exp(E/RT - \alpha MC -$ $\alpha' GC - \beta SME)$	$E/R = 5860$; $\alpha = 10.9$; $\alpha' =$ 4.7 ; $\beta = 5.9 \times 10^{-3}$
Berzin et al., 2007 [129]	Wheat starch	Inline (TSE+DCD)	73–113	MC: 29–40 (d.b.)	–	10^0 – 10^3	$K = K_0 \exp\{n[E/R(1/T - 1/T_0)$ $- \alpha(MC - MC_0) - \beta(SME -$ $SME_0)]\}$	$E/R = 5150$; $\alpha = 10.91$; $\beta =$ 0.0028 ; $K_0 = 1920$; $n = 0.53$; $T_0 = 363$ K; $MC_0 = 0.4$; $SME_0 = 325$
Della Valle et al., 2007 [103]	Wheat starch	Pre-shearing	95–155	MC: 16 (w.b.) GC: 23–32 (w.b.)	–	10^{-1} – 10^4	$K = K_0 \exp\{n[E/R(1/T - 1/T_0)$ $- \alpha'(GC - GC_0)]\}$	$E/R = 14530$; $\alpha' = 25.1$; $K_0 =$ 8080 ; $n = 0.28$; $T_0 = 498$; $MC_0 = 0.27$

Sandoval and Barreiro [99]	Maize starch	Off-line (Plunger-type capillary)	85–120	MC: 27–37 (w.b.)	Starch was processed in the rheometer.	10^2 – 10^4	$K = K_0 \exp(E/RT - \alpha MC)$	$E/R = 1435$; $\alpha = 0.05072$; $K_0 = 12.06$; $n = 0.16$
Tajuddin et al. 2011 [135]	Waxy maize starch	MPR	90–130	MC: 28–44 (d.b.) GC: 14–66 (d.b.)	Steady molecular and rheological state was achieved before measurements.	10^1 – 10^3	$K = K_0 \exp(E/RT - \alpha MC - \alpha' GC)$ $n = n_0 + \alpha_1 T + \alpha_2 MC + \alpha_3 GC + \alpha_{12} T \cdot MC + \alpha_{13} T \cdot GC + \alpha_{23} MC \cdot GC + \alpha_{123} T \cdot MC \cdot GC$	$E/R = 7396$; $\alpha = 17.15$; $\alpha' = 5.564$; $K_0 = 0.03073$; $\alpha_1 = 0.03180$; $\alpha_2 = 20.09$; $\alpha_3 = 37.76$; $\alpha_{12} = 0.04444$; $\alpha_{13} = 0.09083$; $\alpha_{23} = 70.84$; $n_0 = -13.03$

SSE: single-screw extruder; TSE: twin-screw extruder; CDV: capillary/cylindrical die viscometer; SDV: slit die viscometer; DCD: double-channel die; d.b.: dry starch basis; w.b.: wet starch (starch and water) basis; n : power-law index; K : consistency coefficient ($\text{Pa} \cdot \text{s}^n$); E/R : reduced flow activation energy (K); T : temperature (K); MC: moisture content; GC: glycerol content; SME: specific mechanical energy ($\text{kWh} \cdot \text{t}^{-1}$); W : mechanical energy ($\times 10^8 \text{ J/m}^3$ or kJ/kg); P_b : barrel (die entrance) pressure; N : screw speed; ns: no significant effect in a 5% confidence interval. For plasticiser content, either d.b. or w.b. is not indicated when no such indication was given in the published paper.

Tab. 4 Effects of additives on shear viscous properties of starch polymer melt at temperature of 160 °C [108]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

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Additive	Wt %	Consistency, K (Pa·s ^m)	Power-law index, n
Control	–	38,900	0.43
TEG	2	21,400	0.48
TEG	5	14,100	0.48
Urea	2	25,700	0.45
Urea	5	26,900	0.41
GMS	2	36,300	0.40
GMS	5	50,100	0.39
Lecithin	1	8,300	0.67
POES	1	11,220	0.56

TEG: triethylene glycol; GMS: glycerol monostearate; POES: polyoxyethylene stearate.