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

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ABSTRACT

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

Keywords:
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, methylenediphenyl 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-CO$_2$, 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-Landle-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

$\Gamma$, torque

$\dot{\epsilon}$, extensional rate

$\eta_{T_g}$, shear viscosity at glass transition temperature

$\eta_0$, shear viscosity at zero shear rate

$\eta_{add}$, theoretical shear viscosity calculated by the log-additive mixing rule

$\eta_e$, extensional viscosity

$\eta_{exp}$, experimented shear viscosity

$\eta_p$, planar extensional viscosity

$\eta_s$, shear viscosity

$\eta_u$, uniaxial extensional viscosity

$\lambda$, is the relaxation time

$\sigma$, surface tension (foam)

$\tau_0$, yield stress in Herschel-Bulkley model

$\tau_{11}$, 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. Introduction

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

[Insert Fig. 1 here]
The rheology of starch polymers, however, is not a simple issue. While water acts as a destructuring agent and an efficient but volatile plasticiser during processing, most rheometers cannot preserve the water content, which makes the rheological measurements often impossible. Secondly, the massive macromolecular changes under thermomechanical treatment during rheological measurement result in subsequent changes in rheological properties which are difficult to follow. This is in contrast to a standard synthetic polymer like polyethylene (PE), which is relatively stable during processing and measurement. Thirdly, the viscosity of starch polymer melt is much higher than that of most synthetic polymers, which also makes the rheological characterisation difficult. The frequent use of different plasticisers and additives for the purpose of reducing the viscosity and improving the processibility further make the rheological properties of starch polymer melts difficult to understand.

In all, these difficulties have led to incorrect or missing information on processing rheology of starch polymers, and this itself can be one of the biggest hurdles in the development of new environmentally friendly starch polymeric materials.

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

2.1. Structures of starch

The starch granule provides the main way of storing energy over long periods in green plants [11]. Starch granules are mainly found in seeds, roots, and tubers, and are from origins such as maize (corn), wheat, potato, and rice. Native starch granules are well known to have multilevel structures from macro to molecular scales, i.e. starch granules (<1 μm~100 μm), alternating amorphous and semicrystalline shells (growth rings) (100~400 nm), crystalline and amorphous lamellae (periodicity) (9~10 nm), and macromolecular chains (~nm) [11-14]. Native starch granules present a concentric 3D architecture from the hilum with a total crystallinity varying from 15% to 45% depending on the particular plant species [15]. Starch is a polysaccharide consisting of D-glucose units, referred to as homoglucan or glucopyranose. The two major biomacromolecules of starch are amylose and amylopectin. Amylose is a sparsely branched carbohydrate mainly based on α(1–4) bonds with a molecular weight of $10^5$–$10^6$ and can have a degree of polymerisation (DP) as high as 600 [11]. The number of macromolecular configurations based on α(1–6) links is directly proportional to the amylose molecular weight [16]. The chains show spiral-shaped single- or double-helices with a rotation on the α(1–4) link and with six glucoses per rotation, where the hydroxyl groups are mainly located toward the exterior of the helices. On the other hand, amylopectin is a highly multiple-branched polymer with a high molecular weight of $10^7$–$10^9$. It is one of the largest natural polymers known [11]. Amylopectin is based on α(1–4) (around 95%) and α(1–6) (around 5%) links, with constituting branching points localised every 22–70 glucose units, generating a kind of grape-branch-like structure with pending chains of DP $\approx$ 15. This specific structure has a profound effect on the physical and biological properties [11,13].
Besides, in starch granules are also found very small amounts of proteins, lipids and phosphorus depending on the botanical resource [12,13]. These components can interact with the carbohydrate chains during processing (e.g. Maillard reaction) and then modify the behaviour of the starchy materials. The highly hydrophilic nature of starch is by the cause of the abundance of hydroxyl groups in the polysaccharides by genetic selection.

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

[Insert Tab. 1 here]

2.2. Gelatinisation/melting of starch

When native starch granules are heated in water, their semicrystalline nature and 3D architecture are gradually disrupted, resulting in the phase transition from an ordered granular structure into a disordered state in water, which is known as “gelatinisation” [18-20]. Gelatinisation is an irreversible process that includes, in a broad sense and in time/temperature sequence, granular swelling, native crystalline melting (loss of birefringence) and molecular solubilisation [21]. Full gelatinisation of starch under shearless conditions requires excess water, which Wang et al. [22] have defined as >63% for waxy maize starch for example. If the water concentration is too high, the crystallites in starch might be pulled apart by swelling, leaving none to be melted at higher temperatures. If the water concentration is limited, the swelling
forces will be much less significant and the steric hindrance is high. Thus, complete
gelatinisation will not occur in the usual temperature range [23-25]. However, as the
temperature increases, starch molecules will become progressively more mobile and
eventually the crystalline regions will be destructured [26]. The process of
gelatinisation with a low water content could more accurately be defined as the
“melting” of starch [24].

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

3. Starch processing

3.1. Processing strategies

The techniques that have been used to process starch polymers, such as internal
mixer, extrusion, injection moulding, compression moulding, and film casting, are
similar to those widely used for standard synthetic thermoplastics. Among these
techniques, extrusion is the most widely used. A single-screw extruder (SSE) can
handle the high viscosity of starch and provide a high processing pressure for
continuous metering of starch through die shapes. A twin-screw extruder (TSE) has a
large operational flexibility (individual barrel zone temperature control, multiple
feeding/injection, and screw configuration for different degree of mixing/kneading)
and is useful for intensive mixing and compounding of components into starch
plastics. Another advantage of TSE is to allow the decoupling of die flow and
mechanical treatment. In both SSE and TSE, residence times and specific mechanical
energy (SME) inputs can be controlled, and high efficiency production can be
achieved. Other processing techniques such as film blowing and injection moulding
are often combined with extrusion. More details about the specifics of processing
techniques for starch polymers can be found in another review paper [1].

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

Various lubricants have been used to improve the processibility of starch
polymeric materials, such as magnesium stearate [45], calcium stearate [46], and
fluoro-elastomers [43]. The use of a lubricant during processing can reduce the
tendency of the material to stick to the die and clogging it.

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

3.2. Issues related to processing

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

4. Rheometry for starch polymers

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

4.1. Backgrounds

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

Regarding the rheology of starch polymer melts, most literature has dealt with steady shear viscosity (η_s), which can be measured by forcing a polymer melt through a capillary/cylindrical die viscometer (CDV) or slit die viscometer (SDV) and calculated based on the melt flow rate and the pressure drop across the die channel. A SDV is preferably used since pressure transducers can be more easily flush-mounted along the channel and thus pressure gradient (dP/dL) along the channel can be obtained. In this case, the obtained result is more accurate than that from a CDV where only inlet pressure is usually measured and the excess pressure drop is accounted for by Bagley correction [72,73].
Comparing with shear viscosity, extensional viscosity ($\eta_e$) has been much less focused for starch polymers. It can be obtained from entrance pressure drop measurement made on a CDV or SDV [74-76]. The entrance pressure can be determined either from Bagley plots when a CDV is used, or by subtracting the extruder barrel head pressure with the extrapolated pressure at the entrance of the die when a SDV is used. Different analysis methods in extensional flow have been compared for starch polymer melts [77,78]. It has been suggested that extensional viscosity can be used to evaluate the elastic properties of polymer melts [71,74].

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

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

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

4.2. “Off-line” rheometry

As previously stated (Section 3), the most efficient way to process starch is by single-/twin-screw extrusion. After extrusion processing, the rheological properties of TPS can be tested at desired conditions in a separate facility. This is defined here as
“off-line” rheometry, understood as “off the initial extrusion processing line”. In terms of the measurement principles, the category includes rotational rheometer, plunger-type capillary/slit rheometer, and extruder-type capillary/slit rheometer.

4.2.1. Rotational rheometer

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

4.2.2. Plunger-type capillary/slit rheometer

A plunger-type capillary/slit rheometer consists of a barrel where the material is loaded, a plunger (also piston) for compressing and pushing the material, and a capillary/slit die which is attached at the end of the barrel. After the material is loaded into the barrel and melted at a desired temperature, the plunger can move towards the
die at a series of pre-selected speeds. The material is thus forced through the die channel. The flow rate can be calculated with the plunger speed along with its geometry data. The total pressure drop through the barrel and capillary can be calculated with either the load on the plunger or a pressure transducer mounted on the barrel. Alternatively in some latest designs (e.g. Instron® CEAST SmartRheo Series), the \( \frac{dP}{dL} \) can be calculated by a series of pressure transducers flush-mounted through a slit die channel. Consequently, shear rate and shear stress, and thus viscosity, can be calculated. Particularly, some recent developed rheometers (e.g. Malvern® Rosand) have twin-bore units which allows simultaneous measurements on both long and short dies to determine the inlet pressure drop at the die, and therefore the absolute viscosity by Bagley method. On the other hand, when some specially designed dies such as zero-length die were used, the kind of rheometers can be employed to estimate the extensional flow characteristics of polymer samples.

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

In some studies [97-99], this rheometer has been directly used as a processing tool, in which native granular starch pre-blended with plasticiser is only applied with high temperature and high pressure. The problems with this method are the SME is rather
low or even absent, and that heat diffusion is not uniform. Thus, a homogeneous
molten state of starch can hardly be achieved like in extrusion processing.
A pre-shearing rheometer called “Rheoplast®” has been designed for the
rheological studies of starch polymer melts [100-103]. The schematic representation
of this rheometer is shown in Fig. 3. It combines the features of a Couette rotational
system, in which a mechanical treatment may be applied and the melting is executed,
and of a capillary rheometer in which the viscosity is measured. The main advantages
of the Rheoplast include [100,101]:

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

Vergnes et al. [101] claimed that Rheoplast can be as a useful tool for the
simulation of the processing in an extruder because the treatment intensity in the
Rheoplast (rotation speed: 200–700 rpm; melt temperature: 140–180°C; shearing time:
5–40 s) are of the same order of magnitude as those encountered in extrusion
processing. However, Martin et al. [84] found that the viscosity measured by in-line
viscometer is lower than that by Rheoplast due to the difference of SME leading to
different macromolecular degradation.

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

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

4.2.3. Extruder-type capillary/slit rheometer

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

Due to the set-up, this technique usually requires a relatively large amount of
sample for a test compared to a plunger-type capillary/slit rheometer. However, it can
work more efficiently because the extrusion is carried out in a continuous way without
waiting time for sample melting. Besides, this technique is suitable when multiple
extrusion runs are required especially for TPS blends and composites [52,54].
Furthermore, this technique also allows some post-extrusion processes such moisture
content conditioning to be carried out before the rheological measurements [65,108].
The use of a separate extrusion run for rheological measurement, however, may
increase the macromolecular degradation especially with starch which is highly
sensitive to the thermomechanical history [65]. Therefore, the measured viscosity of
TPS by this method was usually lower than by an in-line extrusion rheometer
(discussed in Section 4.3) [43,84]. Besides, the change in screw speed for different
shear rates also changes the processing history, which results in different product to
be tested at different shear rate. However, in a some particular studies, the shear rate
was controlled by a speed-controlled piston in the die [106] or a side-stream valve at
the end of the extruder barrel [105], which greatly reduced the thermomechanical
history difference. Since the latter method has mostly been used in an in-line
rheometry, the details will be discussed in Section 4.3.2.

4.3. “In-line” rheometry

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

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

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

Many studies have shown that the operation of the in-line viscometer has a considerable effect on the rheological properties of starch [24,93,111,113,117,119] due to the granular transformation and macromolecular degradation. To correct these effects, some authors have proposed the viscosity models involving the dependence of strain history [97], SME [84], and starch conversion [113], which could be extended to other systems. However, the models depending on an extrusion operating variable
such as screw rotation speed [93] cannot be generalised for other systems. These models are detailed in Section 5.1.6.

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

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

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

[Insert Fig. 5 here]

As a result of such design, the Rheopac permits the variation of the shear rate in the measuring section without modifying the flow conditions along the extruder, so that the material undergoes the same thermomechanical history. Another great advantage of this rheometer is that measurements can be performed more swiftly than with a classical slit die, since no waiting time for the stabilisation of the melt flow is required after adjusting the piston height for different shear rate [120]. However, it has been suggested that each channel of the Rheopac is only be partially obstructed by the piston since starch overcooking and die fouling would happen in case of fully closed channels.
Li et al. [130] also used an in-line SDV for the rheological study of TPS. There was an adapter fitted between the SDV and the extruder to allow the diversion of flow. Both the flow restriction towards the bypass channel and the one towards the SDV could be controlled by two valves for each of them. By adjusting the openings of the two valves, the flow rate in the SDV was varied to achieve different shear rate. Instead of calculating the relationship between the two valve openings (which is used for the Rheopac [120]), there was a pressure transducer mounted before the two valves, which could be used to monitor and maintain the entrance pressure \( P_0 \) at a constant value while adjusting the valve openings. Therefore, it possesses the merits of the Rheopac while it is more convenient to use.

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

\[
    n = \frac{\log \left( \frac{L_S}{L_L} \right) + \log \left( \frac{r_L}{r_S} \right)}{\log \left( \frac{Q_L}{Q_S} \right) - 3 \log \left( \frac{r_L}{r_S} \right)}
\]

where \( L, r, \) and \( Q \) are respectively the length, radius, and volumetric flow rate of a capillary, with the subscript “S” means the small one and “L” means the large one. This method provides a more accurate and time efficient determination of the \( n \) value.
than any other in-line methods. However, due to the geometry restrictions, pressure transducers at the entrance to the bifurcated flow channels and along these channels was not possible, and therefore this rheometer was not suitable for the determination of the $K$ value.

[Insert Fig. 6 here]

4.4. Others types

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

4.4.1. Multipass rheometer

A multipass rheometer (MPR) has recently been developed for the rheological measurements of liquids and polymer melts [132-134]. Tajuddin et al. [135], for the first time, used a MPR for the study of rheological properties of TPS. Fig. 7 gives a schematic representation of the MPR. It consists of a top and a bottom barrel in which two servo-hydraulically driven pistons enter respectively. A capillary test section is positioned between the barrels. The temperature of the barrels and capillary can be accurately controlled, and the pressures in the barrel sections are monitored. After introduction of the material, one piston will be moved toward the other until a specific hydrostatic pressure is achieved. The two pistons are then synchronously
driven such that their separation remains constant. In “multipass steady” mode, the
pistons advance at constant velocity for a given time, yielding steady shear data. The
piston position is then held constant for a set dwell time and then the piston motion is
reversed. In this way, a multitude of successive steady flow measurements can be
made. Mean differential pressure can be calculated at certain piston speed. Bagley
correction can be applied by using capillaries with different \(L/r\) ratios [72]. Different
piston speeds are used for obtaining the result at a wide range of shear rates. Thus,
the viscosity can be calculated.

[Insert Fig. 7 here]

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

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

As a relatively new rheometer, MPR has not been fully employed for starch
polymer melts. Since MPR can also be operated in an oscillatory mode [133], it could
provide a reliable method for studying dynamic shear viscoelastic properties.
Furthermore, it has also proven useful in studying viscous conditions favouring bubble growth in polymer melts [136].

4.4.2. Mixer-type rheometer

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

In some studies [31,32,52], such a mixer was used to investigate the transformation of native granular starch into a thermoplastic form, which could be followed by the change in torque with time. When the torque value reached a stable value, it was considered that a stable state of TPS is achieved under specific processing conditions (initial temperature and rotor speed). In another study [137], the focus was on the rheological properties of TPS fully developed in the mixer under different moisture and temperature conditions. In order to convert the torque into a stress value and the rotation speed into a shear rate value, the flow curve of a well
characterised molten polymer was used and the empirical correlation through a classical least square procedure is practised. An alternative method involves the assumption of the flow in the Rheomix device to be in a double Couette system [138]. It has been reported that, though wide shear rate range \((10–1000 \text{ s}^{-1})\) could be obtained by Rheomix, heat generated by viscous dissipation in high shear rate range can hardly be evacuated through the chamber cooling system, and this may result in large discrepancies on the results [137].

5. Processing rheology of starch polymeric materials

5.1. Steady shear viscosity

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

\[
\eta_s = K\dot{\gamma}^{n-1}
\]

where \(\dot{\gamma}\) is the shear rate and \(K\) is the consistency coefficient. The \(n\) value lower than 1 means the shear thinning behaviour of starch polymer melts, which is mainly ascribed to the gradual reduction of molecular entanglement at increased shear rate. The more the \(n\) value approaches 1, the more the melt behaves like a Newtonian fluid, which means it is less sensitive to shear rate. Based on Eq. 3, many authors have focused on the effects of those formulation (plasticiser type and content) and processing parameters (SME, temperature, etc.) on \(n\) and \(K\) in their studies. Thus, different empirical equations describing \(n\) and \(K\) based on different systems have been proposed, which are summarised in Tab. 3. However, it may be difficult to make
direct comparisons of these models especially their constants due to the differences of
samples and measurement methods and conditions. Therefore, the effects of
thermomechanical treatment, temperature, plasticiser/additive, starch type/structure,
additives, and blends/composites will be discussed in detail respectively in the
following sections. Then, the shear viscosity models will be further discussed.

[Insert Tab. 3 Here]

5.1.1. Effect of thermomechanical treatment
During processing, starch could undergo different degrees of granular
transformation and of macromolecular degradation under thermomechanical treatment;
thus, actually different products with different rheological properties may be obtained.
To understand the effects of processing on the shear viscous properties of starch
dec polymer melts, in-line methods have been most frequently utilised
[58,77,84,93,97,111-113,117,119,120,123,126,127,129-131]. Besides, pre-shearing
[100] and off-line rheometers [106] have also been used.
It has been reported that increasing the screw speed could reduce the melt
viscosity for both in-line [93,112,123] and offline [106] rheometric systems.
Particularly, when a TSE was used (shear rate was controlled by the feed rate), the
increase in screw speed, though reduces the degree of fill and the mean residence time,
increases the intensity of mechanical treatment, which results in greater granular
transformation and macromolecular degradation and thus lower melt viscosity; and
this mechanical treatment was more important at lower temperature [93]. Besides, an
increase in feed rate for TSE can also provide a greater thermomechanical treatment
due to the increase in the compression of material inside the extruder. However,
when the feed rate is too high, the thermomechanical energy that a specific amount of material received would reduce, resulting in a lower degree of starch transformation and thus higher viscosity [130].

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

It has been unanimously agreed that higher SME input can result in a greater starch granular transformation and macromolecular degradation (as demonstrated by intrinsic viscosity and SEC profile) [58,106,120,127,129], both of which lead to the decreased viscosity of starch polymer melt. Martin et al. [84] observed a linear relationship between K and SME in a single-logarithmic plot [Fig. 8]. However, the manner in which SME influences viscous properties can be different under different conditions. Using a pre-shearing rheometer for starch with 28% moisture content and at 110 °C or 150 °C temperature, Vergnes and Villemaire [100] observed that, while
higher SME led to a lower viscosity (lower $K$ value), the $n$ value was not affected. They also observed that the effect of thermomechanical treatment is more or less marked according to the temperature [100]. In another study where a Rheopac rheometer incorporated to a TSE was used, Vergnes et al. [120] reported that a change in SME from 180 to 241 kWh/t by varying the feed rate can result in the great changes in both $K$ from 9050 to 2610 Pa.s$^n$ and $n$ from 0.35 to 0.52 for the TPS at moisture content of 16.7% and temperature of 190 °C.

[Insert Fig. 8 here]

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

5.1.2. Effect of temperature

By using an in-line system, some authors have studied the effect of temperature during processing, which can affect the changes in starch, and thus the melt viscosity. For example, Li et al. [113] found that the maximum apparent viscosity occurred at 120–140 °C barrel temperature for all different shear rates. They suggested that the
increase in melt viscosity at $\leq 130$ °C is due to the increase in starch gelatinisation, whereas the decrease in the melt viscosity at $\geq 130$ °C indicated that starch degradation occurred. Here, it needs to be pointed out that, in most studies by an in-line system, it is difficult to differentiate the effect of temperature on starch granular transformation and macromolecular degradation and their effects directly on reducing the viscosity of starch as a polymer. Furthermore, when reading the literature on the in-line rheology of TPS, one should take note of what kind of temperature was used as a varied parameter: the temperature at the last barrel zone(s) and die (processing temperature) [93,112,119,130], or the melt temperature at the die channel (testing temperature) [58,84,113,120,127,129,131]. In the former case, the melt temperature may be higher than the controlled temperature because of the viscous dissipation (discussed in Section 5.4). Thus, misleading rheological results may be generated. In the latter case, it was common to achieve different desired melt temperatures by varying the temperatures of barrel zones and die, of which the details, however, were often missing. On the other hand, it is a remarkable that, even if an off-line system is used, the temperature of the second measurement run may still have some “processing” effect. Willett et al. [108] indicated that, when the measurement temperature was high (160 or 180 °C), significant macromolecular degradation could occur during the testing phase, to the point that any effects of starting materials were eliminated.

In the following in this section, the temperature effect on melt viscosity in terms of thermal activation of melt flow will be discussed. It is well known that an increase in temperature would result in a lower viscosity of starch polymer melt. According to Eq. 3, this can be reflected by a lower value of $K$ at higher temperature as widely reported in the literature [40,44,49-51,58,65,84,90,91,94,100,106-108,110,113-]
However, there have been discrepancies over the effect of temperature on the $n$ value. In some especially early studies [99,108,110,113,114,116,118,129,137,139], the $n$ was assumed to be a constant in the shear viscosity models; thus, the effect of temperature on $n$ was not elaborated. By drawing the shear viscosity versus shear rate curve in a double-logarithmic plot, other researchers observed that an increase in temperature would cause a higher $n$ value [58,65,94,100,107,115,122,127,135]. The same trend has been observed for starch/PLA blends [49-51]. In the meantime, there have been reports showing that no clear influence of temperature on $n$ for starch polymer melts [44,84].

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

5.1.3. Effect of plasticiser/additive

Plasticisers usually have a large influence on the shear viscous properties of starch polymer melts. In most cases, plasticiser is blended into native granular starch before processing. As a result, the plasticiser content would not only influence the granular transformation and macromolecular degradation during processing, which affect the viscosity, but also assist the movements between starch inter- and intra-molecular chains, which reduce the viscosity as well. Particularly, Willett and co-workers [65,108] was able to separately determine the effects of moisture content during processing and during measurement by using an off-line system. In one study [108], starch was pelletised at different moisture contents during the first run and then equilibrated to the same moisture content for shear viscosity measurements. It was shown that moisture content during the pelletising step had a significant impact on melt viscosity when tested at low temperature (110 or 130 °C): the TPS sample pelletised with 15% moisture content had the lowest viscosity, that pelletised with 20% moisture content had the highest, while that pelletised at 30% moisture content had an intermediate value. The reasons could be that the high melt viscosity (during processing) at 15% moisture content caused more shear stress and more chain scission, while water catalysed hydrolysis might occur with high moisture content (30%). In the other studies [65,108], TPS pellets were prepared at the same moisture content and subsequently equilibrated them to different moisture contents for shear viscosity measurements.
Apart from the effect on starch granular transformation during processing, an increase in plasticiser content would decrease the viscosity of starch polymer melt since it can decrease the polymer entanglement density and increase the ease of disentanglement. It has been well demonstrated that a higher amount of water would result in a lower $K$ value \cite{57,58,65,84,93,94,99,100,107,108,110,111,113-119,122,127,129,137,139,140}. However, the effect of moisture content on the $n$ was unknown in many studies since it was taken as a constant for modelling \cite{57,93,99,99,110,111,113-119,129,137,139,140}. In other reports where the $n$ values were shown at different moisture content, an increase in $n$ with increasing moisture content was mostly observed \cite{58,65,94,100,107,111,115,127} although there have also been reports where no evident trend of $n$ with the change in moisture content could be justified \cite{45,84,122,131}.

As a frequently used plasticiser for starch, glycerol reduces the viscosity of starch polymer melts as evidenced by a lower $K$ value \cite{41,106}. The impact of glycerol content on $n$, however, has been in disagreement especially based on the limited published data. While Thunwall et al. \cite{96} reported an unchanged $n$ value with increasing glycerol content for hydroxypropylated oxidised potato starch, Rodriguez-Gonzalez et al. \cite{41} observed a higher glycerol content slightly reduced the $n$ value for wheat starch. Regarding the latter result, it could be possible that when the glycerol content is lower, less degree of starch granular transformation occurs during processing, and the remnant large amount of starch granules make the fluid behave more like a filled polymer melt. As a result, higher $n$ value is displayed. Otherwise, a higher $n$ value should be expected with increasing glycerol content, and this has been verified through rheological modelling \cite{84,135}.
By MPR, Tajuddin et al. [135] investigated the shear viscous properties of well-transformed waxy TPS melts plasticised by both water and glycerol. The results showed that an increase in glycerol/water ratio (1:4, 2:3, and 3:2) resulted in a stronger shear-thinning behaviour; however, total plasticiser content (70–110%) had little influence on $n$ (cf. Fig. 9). It was thus proposed that, different structural characteristics can result with different plasticiser (cf. Fig. 10): when plasticised mainly by water, amylopectin molecule has a compact ellipsoidal conformation by greatly unfolding their branches, and these “ellipsoids” are easy to move, so more Newtonian-like behaviour is shown; the “ellipsoids”, however, are largely absent when glycerol is the main plasticiser, and the amylopectin molecules behave more like a standard polymer and show stronger shear-thinning behaviour.

Many other low molecular weight substances such as citric acid, formamide, and urea have also been utilised as plasticisers for starch. Citric acid can form stronger hydrogen bonding interactions with starch molecules than glycerol [40]. It weakens the interaction of starch molecules and improves the plasticisation of starch [91]. Further, it may also depolymerise starch molecules during processing [49]. As a result, citric acid can obvious reduce the viscosity of starch polymer melts, though its effect on $n$ has not been well understood [40,49,91]. On the other hand, plasticisers such as formamide and urea are also effective plasticisers since their amide groups enable them to form strong hydrogen bonds with starch and to break the existing hydrogen bonds in starch [44,90,92]. Such strong interaction allows formamide to be
used to plasticise starch even without water [51,92]. Wang and co-workers [51,92] examined the effect of formamide/glycerol ratio on the shear viscosity of TPS at fixed total plasticiser content, and showed that an increase of formamide/glycerol ratio decreased the $K$ value but increased the $n$ value. Nevertheless, when 30% (dry basis) of the mixture of formamide and urea was used as plasticiser, TPS could have a higher shear viscosity and a lower $n$ value than that plasticised by the same amount of glycerol [90]. In another study, with the increase of formamide-urea mixture from 30 to 50%, the $n$ value first decreased and then increased [44]. Considering the whole of the mixture plasticiser could be effectively bound to starch at 40% level [44], it can be considered that, before 40%, the increase of plasticiser content resulted in more hydrogen bonds which reduced the “ellipsoids” in starch and cause a stronger shear thinning behaviour (cf. Fig. 10); however, when the plasticiser content was higher than 40%, the excess of plasticiser reversed the trend due to its Newtonian behaviour. Moreover, the authors of all these studies have shown that the use and higher content of formamide, urea, and/or citric acid comparing with glycerol could generally cause a decrease in flow activation energy ($E/R$, cf. Eq. 4 in Section 5.1.6), indicating less temperature-sensitivity of TPS plasticised by these plasticisers [40,44,49,51,90-92].

Willett et al. [108] investigated the effects of various low molecular weight additives such as urea, lecithin, triethylene glycol (TEG), glycerol monostearate (GMS), and polyoxyethylene stearate (POES) on the shear viscosity of TPS, and the results are summarised in Tab. 4. It was found that all additives except GMS significantly lowered the melt viscosity of TPS, with lecithin and POES exhibiting the greatest efficiency (decreasing $K$ and increasing $n$), though lecithin could effectively reduce the molecular degradation of starch as well. Relative to the melt with 15% moisture content, all the additives except GMS were more effective than additional
water at reducing viscosity, which can be ascribed to the strong interactions between these additives and starch molecules. The melt viscosity with GMS was essentially the same as, or slightly higher than, those of starch/water, and this behaviour could be attributed to the presence of unmelted amylose–lipid complexes in the melt. Though amylose–lipid complexes could also form in the samples plasticised by lecithin and POES, they were most likely melted at the testing temperature (160 °C) and thus had no apparent effects on the rheological results.

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

Supercritical carbon dioxide (sc-CO\textsubscript{2}), which has been considered as a novel plasticiser in extrusion processing [142], also has an impact on the rheological properties of starch polymer melts. Recently studies [124,143] have shown that the use of sc-CO\textsubscript{2} during extrusion processing lead to a lower $K$ and a higher $n$ for TPS melt. This is because sc-CO\textsubscript{2} can solvate starch molecules and reduce polymer entanglement and subsequently decreased shear-thinning behaviour and viscosity. As a result, sc-CO\textsubscript{2} has a great potential for improving the processibility of starch polymer melt.

Though a lubricant is an important additive in practical processing of starch polymers, there have been few studies dealing with the effect of lubricant on the shear
viscous properties of starch, expect that Thuwall et al. [43] showed that the addition
of 3% fluoride elastomer lubricant to glycerol-plasticised amylose-rich potato starch
had no significant effect on melt viscosity.

5.1.4. Effect of starch type/structure

By using pre-shearing rheometer, Della Valle et al. [103] have shown the
difference of rheological properties of TPS melts from different botanical origins. For
example, smooth pea and wheat starches have the same $n$ value, which is slightly
higher than that of potato starch. By rheological modelling, they also showed that the
shear viscosity of smooth pea starch has a greater dependence on temperature than
any other types. On the other hand, starches with different amylose/amylopectin
ratios but from the same botanical origin have attracted particular scientific interests
as they display different processing and product properties. Previous studies [42,144-
153] have shown that polymeric materials based on high-amylose starch exhibit
superior strength and toughness; however, the extrusion processing of high-amylose
starch is much more difficult than that of low-amylose starch, partly due to the higher
die pressure and torque requirements as results of the higher melting temperature and
viscosity of the former [23,154,155]. Della Valle et al. [127] and Xie et al. [107]
systematically investigated the shear viscous properties of maize starches with
different amylose/amylopectin ratios and both groups found that the higher the
amylose content, the higher is the shear viscosity and the more pronounced is the
shear-thinning behaviour, under the same shear rate range (Fig. 11). This is also the
case for potato starch [43] and wheat flour [98]. As discussed before, amylopectin
mainly has clusters composed of short chain branches (DP $\approx 15$); and, despite its high
molecular weight, it has a compact ellipsoidal conformation which reduced its ability
to create entanglements, resulting in a lower viscosity [107,127]. In contrast, the long linear chains of amylose cause more entanglements between macromolecules, which increases zero shear viscosity and enhanced non-Newtonian behaviour. In addition, the high viscosity of high-amylose starch can also be attributed to its lower tendency to undergo granular transformation [23] and macromolecular degradation [66].

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

5.1.5. Effect of blending/compositing

Generally, blending starch with another polymer would produce an average viscosity. This has been measured in the starch-based blends mostly with PCL [53,54,89], PLA [49,50,52], and PVA [56,57] as well as with other synthetic polymers [105]. It should be noted that, in some studies [49,50,52-54,57,89], the viscosity of TPS was higher than that of the second polymer phase, while a reverse pattern was observed in other studies [47,51,56]. This largely depends on the measurement
temperature and the plasticiser(s). For example, Xie observed that an increase in starch/PLA ratio could increase the viscosity of the blend at temperature of 180 °C, whereas Sarazin et al. [47] found that adding starch (with 24 or 36% glycerol content) to PLA could reduce the viscosity of PLA at temperature of 165 °C. The influence of blending on the $n$ value follows the same pattern. Since the $n$ value of TPS is usually lower than that of the second polymer used due to its stronger shear-thinning behaviour, blending usually results in a higher $n$ value [49,50,52,57]. However, care should be taken when explaining the viscous results of starch-based blends since other more factors can also affect the viscosity of the blends. For instance, Wang and co-workers [49,50] found that the $K$ value of starch/PLA was even lower than both those of TPS and PLA. They suggested the reason to be the depolymerisation effect of citric acid (which, along with glycerol, was used as plasticiser for TPS) for both starch and PLA in the blend. In another study, Wang et al. [51] discovered that there were large differences in the $K$ and $n$ values of starch/PLA blends without or with water as one of the plasticisers. With 10% moisture content in addition to formamide and glycerol, the blend showed a lower $K$ and a higher $n$. The $n$ value of starch/PLA blend with water was even higher than that of pure PLA. This may due to the molecular weight degradation of PLA during processing with the presence of moisture in starch.

Kalambur and Rizvi [89] studied the shear viscous properties of TPS/PCL blends prepared by both standard extrusion blending and reactive extrusion (REX) blending. By the latter method, added were hydrogen peroxide ($\text{H}_2\text{O}_2$), which help the cross-linking between starch and PCL molecules, and nanoclay (Nanocor® I.30E organoclay), which reinforced the composite. They found lower $n$ and $K$ values for reactive blended sample compared with that of normally blended sample. This was
attributed to the depolymerisation of starch molecules by oxidation reactions. They also observed that an increase in nanoclay content could increase the $K$ value or shear viscosity at low shear rates. A similar result of $K$ was found by Ma et al. [90] who investigated the effect of the addition of fly ash into TPS on the shear viscosity of the composite. However, both studies didn’t show a clear trend of the effect of the filler content on the $n$ value.

5.1.6. Shear viscosity models

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

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

(4)

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

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

(5)

with $T_0$, $MC_0$, $GC_0$, and $SME_0$ as reference conditions. In addition, some models consider screw speed [93] during processing as well; however, they are not widely utilised since the impact of the screw speed largely depends on the machine characteristics and can be more easily be reflected by SME. Though the degree of starch transformation (which can be measured by iodine or differential scanning calorimetry (DSC) method), has also been introduced into the model by some authors [113], it is actually not an operating term and thus the resulting model has poor
applicability in practical processing. Besides, no simple relationship between starch transformation and shear viscosity should be expected and further study is needed [31,32].

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

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

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

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

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

$$n = n_0 + \alpha_1 T + \alpha_2 MC + \alpha_3 GC + \alpha_4 SME + \alpha_12 T \cdot MC + \alpha_13 T \cdot GC + \alpha_14 T \cdot SME +$$

$$\alpha_23 MC \cdot GC + \alpha_24 MC \cdot SME + \alpha_34 GC \cdot SME + \alpha_123 T \cdot MC \cdot SME + \alpha_124 T \cdot MC \cdot SME +$$

$$\alpha_134 T \cdot GC \cdot SME + \alpha_234 MC \cdot GC \cdot SME + \alpha_1234 T \cdot MC \cdot GC \cdot SME \quad (7)$$

where $n_0$ and $\alpha$ are constants. Actually, not all of these parameters ($T$, $MC$, $GC$, and
SME) were used in a single study in literature, so the reported models were actually simpler.

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

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

$$\eta = \frac{\tau_0}{\dot{\gamma}} + K\dot{\gamma}^{n-1}$$  \hspace{1cm} (8)

where $\tau_0$ is the yield stress. The existence of a yield stress generally indicates a structuration of the material. For starch polymers, this may be attributed to the recrystallisation of starch at rather low shear rate [103].

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

$$\eta = \left[\left(\frac{\tau_0}{\dot{\gamma}}\right)^n + \mu_\infty \dot{\gamma}^{n-\eta}\right]^{\frac{1}{n}} \exp\left[\frac{E}{R \left(\frac{1}{T} - \frac{1}{T_0}\right)} + b(MC - MC_0)\right] \left[1 + A\left(1 - e^{-\psi}\right)\right] \left[1 - \beta(1 - e^{-\phi})\right]$$  \hspace{1cm} (9)

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; $k\psi = \infty$ (indicating very rapid gelatinisation); and $d = -5.87 \times 10^8$; and the reference
conditions are $T_0 = 323.15$ K, $MC_0 = 0.476$ (dry basis). The other parameters can be calculated by:

$$\alpha = \exp\left(18.9 - \frac{6070.6}{T}\right)$$  \hspace{0.5cm} (10)

$$\beta = \exp\left(-6.371 + \frac{2530.5}{T}\right)$$  \hspace{0.5cm} (11)

$$A = \beta(C_s)^\alpha$$  \hspace{0.5cm} (12)

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

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

$$\eta_s = \frac{\eta_0}{\left[1 + (\dot{\gamma}\lambda)^a\right]^{\frac{1}{n}}}$$  \hspace{0.5cm} (13)

where $\eta_0$ is the shear viscosity at zero shear rate, $\lambda$ is the relaxation time (s), and $a$ is the Carreau-Yasuda fitting parameter. The use of this model for starch polymer melts may help in understanding the influence of shear rate on starch structures.

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

Starch polymer melts are commonly considered to exhibit a viscoelastic behaviour. The measurement of elastic component of a starch polymer melt can be associated
with the extensional viscosity ($\eta_e$) and the first normal stress difference ($N_1$).

Compared to shear viscosity, $\eta_e$ and $N_1$ have received minimum attention. The difficulty in their measurement may be part of the reasons [68]. Nevertheless, the study of elasticity of starch polymer melt is crucial due to several reasons:

- Extensional flow is indeed present due to the contraction at the die entrance in extrusion; forces are not only put onto the material due to shear flow, but also to extensional flow.

- $N_1$ and $\eta_e$ are far more sensitive than shear viscosity to the changes or differences in melt microstructure [81,158,159].

- Extensional flow function can also be used to adjust the processing conditions to maintain product performances (e.g. forming [160,161]).

- Extensional flow need to be used to develop and test a “complete” constitutive equation that can be used in modelling the processing operations.

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

Though it has been found in several studies [85,121,162] that the $N_1$ generally increased with shear rate ($\dot{\gamma}$), no accurate relationship between $N_1$ and $\dot{\gamma}$ has established for starch polymer melts. On the other hand, it has been assumed that the power-law dependence of $\eta_e$ on extensional rate $\dot{\varepsilon}$ is applied to starch polymers
\[ \eta_e = S\dot{\varepsilon}^{t-1} \]  \hspace{1cm} (14)

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

Like shear viscosity, \( \eta_e \) can be affected by different processing conditions. It has been observed that increasing moisture content and temperature decreased \( \eta_e \) at higher \( \dot{\varepsilon} \) \([78,122]\). In addition, processing history could greatly influence \( \eta_e \) \([122]\).

However, no modelling work has been done in this aspect.

As \( t \) in Eq. 14 is the ratio of the rate of shear energy dissipation to that of extensional energy dissipation \([76]\), a small value of \( t \) observed for maize meal dough corresponds to the dominance of extensional flow over the shear component \([77]\).

The Trouton ratio, \( T_r \), which is the ratio of the extensional viscosity to the shear viscosity, is more commonly used to evaluate the elasticity of a material. According to Jones et al. \([164]\), in uniaxial extensional flow, \( T_r \) can be expressed as:

\[ T_r = \frac{\eta_u(\dot{\varepsilon})}{\eta_s(\sqrt{3}\dot{\varepsilon})} \]  \hspace{1cm} (15)

where \( \eta_u \) is uniaxial extensional viscosity. And, in planar extensional flow, it can be expressed as:

\[ T_r = \frac{\eta_u(\dot{\varepsilon})}{\eta_s(2\dot{\varepsilon})} \]  \hspace{1cm} (16)
where $\eta_p$ is planar extensional viscosity. In uniaxial extensional flow, $T_r = 3$ is displayed for inelastic non-Newtonian fluids, and $T_r > 3$ for viscoelastic fluids; in planar extensional flow, this critical value is 4. As reported by Bhattacharya et al. [78] for maize meal in uniaxial extensional flow, the $T_r$ values ranged from 25 to 50, as affected by moisture content, barrel temperature, and deformation rate, clearly demonstrate that the extensional viscosity is much higher than the shear viscosity; thus, a significant elastic behaviour was confirmed. Seethamraju et al. [105] reported an increase in starch content in starch/ethylene propylene maleic anhydride (EPMA) blend from 60 to 70\% resulted in a higher $T_r$, again suggesting a stronger elastic property of starch polymer melt.

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

5.3. Dynamic shear rheology

Dynamic shear rheology is another way to characterise the viscoelastic properties of a material. However, due to some difficulties (especially as a result of water evaporation), few reports have used this method for starch polymers. In a study by Della Valle and Buleon [88], the linear viscoelastic behaviours of TPS samples from various origins produced by twin-screw extrusion were studied by parallel plate rheometers in oscillatory mode at 90 and 150 °C. At low strain, the plasticised starch
is found to behave as a viscoelastic gel-like material. This behaviour is partially explained by its semicrystalline structure due to the presence of single-helical amylose structures (similar to the one formed by amylose–lipid helical complexes) formed after extrusion, as evidenced by X-ray diffraction (XRD) results. Crystallites are assumed to participate in the formation of an elastic network, embedded in a viscoelastic amorphous phase. The higher molecular weight of the potato starch is responsible for its larger moduli. In the case of maize starch, the highly branched amorphous amylopectin softens the structured behaviour, resulting in lower moduli compared to those of rich-content amylose.

5.4. Viscous heat effects

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

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

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

5.5. Controlling the processing rheology

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

Shear rate is another important variable to manage the rheological properties of starch polymeric materials. As reported by Kalambur and Rizvi [89], at temperature of 120 °C, the shear viscosity of starch/PCL blend could be lower than that of pure PCL at shear rate higher than 25.2 $s^{-1}$. Another report [48] demonstrated that, when
the shear rate was higher than $10^4$ s$^{-1}$, the shear viscosity of TPS could be reduced lower than that of PLA at 130 °C. Furthermore, Walia et al. [55] plotted the changes in viscosity ratios of TPS and PHEE as a function of shear rate at different moisture and temperature conditions (cf. Fig. 12). The viscosity ratio was found to vary over two orders of magnitude (0.1–10) with the changes in TPS moisture content (15–30%) and temperature (120–160 °C). This information could be used to understand the compatibility of their blend (further discussed in Section 6.1). In practice, shear rate is mostly related to the screw configuration, screw speed, and die geometry in extrusion processing. As a result, increasing screw speed of the extruder may be an effective way to alleviate the problems of the high motor torque and the blockage of starch polymer melt in the extruder and die channels.

[Insert Fig. 12 here]

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

6.1. *Rheology-blend compatibility/morphology relationship*

When considering the blending of two polymers, a practical method is to first compare their rheological properties. If the rheological properties of two polymers differ greatly, intimate mixing and good compatibility should not be expected. Of course, differences in thermodynamics and polarity of starch and the second polymer must also be considered. Often the highly hydrophilic nature of starch is in contrast to the hydrophobicity of the blended polymer, and thus a compatibilising strategy usually has to be employed [2].
A change in compatibility of the blend can be reflected by the change in melt viscosity. It has been shown in several studies [47,49,51,91] that a higher compatibility of starch/PLA blend, which was achieved by plasticiser strategy and demonstrated by a well blended morphology and better dispersion of the phases as observed by scanning electron microscopy (SEM), could be reflected by a lower $K$ value and a higher $n$ value. This is also the case for starch/PE blend [91]; and the same relationship was displayed when the compatibility of starch/PLA was achieved by REX [50]. Xie and co-workers [52,54] investigated the effect of compatibiliser (methylenedipheny diisocyanate, MDI) distribution on the rheological properties of TPS/polyester blends. The polyesters used were PCL, PLA, and PBSA. It was shown that MDI did not clearly affect the viscosity of starch/polyester blends when it was distributed in starch phase. However, MDI increased the melt viscosity and decreased the $n$ value of the blends when it was distributed in polyester phase. This could be linked to the improved compatibility between TPS and polyester as demonstrated by the improved interface in SEM results and the closer melting temperatures of each phase in DSC results. They claimed that controlling the MDI distribution can greatly reduce the consumption of the highly reactive isocyanate group in MDI by the moisture in starch, and thus improve the compatibilising functionality of MDI.

Walia et al. [55] discovered that the viscosity ratio of TPS and poly(hydroxy ester ether) (PHEE), which could be controlled by moisture content of TPS and temperature, had a substantial effect on the size of dispersion, the type of morphologies developed, and the onset and nature of continuity of the starch phase in their blends. Deformation (in the flow direction) of the dispersed starch phase was possible under high moisture conditions (lower viscosity ratio), leading to fibrillar and laminar types of morphologies at 50–80% starch level, whereas processing at a low moisture level
(higher viscosity ratio) produced a more dispersed morphology. When the viscosities
of the two phases were significantly different, the low-viscosity polymer migrated to
the surface. Hence, controlling the plasticiser level and temperature can be an
effective way to tailor the morphology and properties of the blends.

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

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

where $\Phi_{\text{PCL}}$ and $\Phi_{\text{TPS}}$ are the volumetric fractions of PCL and TPS in the blend
respectively. The deviation of experiment value with respect to the predicted value
could then be calculated by:

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

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

6.2. Rheology-expansion/foaming property relationship

The rheological properties of starch melt has a strong influence on the
macromolecular expansion behaviour [168]. Vergnes et al. [101] found that cross-
sectional expansion index (SEI, calculated as the cross-sectional area of the extrudate
divided by the cross-sectional area of the die) of starch polymer melt could be varied by shear rate at the die when the same thermomechanical treatment was imposed. The higher the shear rate, the larger the SEI was observed. This is related to the shear-thinning behaviour of starch polymer melt. A lower viscosity at higher shear rate made the expansion easier, which is in agreement with the bubble growth theory [169]. Ilo et al. [110] discovered that melt viscosity, along with moisture content, had a significant influence on the SEI. The SEI decreased with increasing melt viscosity at higher moisture content, which is in line with bubble growth theory [169]. However, the SEI increased with increasing melt viscosity at low moisture content, which may due to the higher stored energy of starch molecules during their flow through the die at higher melt viscosity [170]. Della Valle et al. [128] found that, for the TPS samples with different amylose contents, volumetric expansion index (VEI, defined by the ratio of the corresponding specific dimension of the extrudate to that within the die, multiplied by moisture correction factor) increased as melt viscosity decreased at given moisture content and temperature. However, it was claimed that higher moisture content, which reduced the viscosity as well, might result in a drop of VEI [128], which cannot be explained by simple bubble growth. Fan et al. [171] developed a model to describe the dynamics of bubble growth and shrinkage in starchy extrudate: a bubble cell first grows by rapid vaporisation of the superheated moisture, and subsequently shrinks by the cooling of vapour which produces a negative pressure difference. The power-law model (cf. Eq. 3 and 4) is used to calculate the shear viscosity of the extrudate in the former stage of bubble growth, with the shear rate of the expanding bubble taken as:

\[
\dot{\gamma} = \frac{\dot{R}}{2R}
\]  

(20)

where \( R \) is the bubble radius and \( \dot{R} \) is the rate of change in \( R \). In the latter stage of
growth, the temperature of the melt will approach the $T_g$ (i.e. $T \leq T_g + 50$), and the
shear rate will be very small; hence, the $\eta_0$ calculated from Williams-Landel-Ferry
(WLF) equations is used to describe the shear viscosity of the extruded melt:

$$\log \frac{\eta_0}{\eta_{r_g}} = \frac{-17.44 \times (T - T_g)}{51.6 + (T - T_g)}$$  \hspace{1cm} (21)

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

$$P_b - P_a = \frac{2\sigma}{R} + 4\eta_0 \frac{\dot{R}}{R}$$  \hspace{1cm} (22)

where $P_a$ is the vapour pressure inside a bubble; $P_a$ is the ambient pressure; and $\sigma$ is
the surface tension. Fan et al. [171] found that melt viscosity is the dominant factor
resisting cell growth and shrinkage, whereas surface tension has negligible effect. It
was also shown that the activation energy, $E/R$ (cf. Eq. 4) had a very strong effect. A
decrease of $E/R$ value, which means lowering the viscosity, gave rise to faster
expansion of a bubble just before its severe collapse; higher viscosity as a result of
higher $E/R$ value delayed the growth, but slight shrinkage was observed because the
low maximum bubble radius obtained reduces the heat and mass transfer area
resulting in a slower drop in temperature and moisture and hence a smaller increase in
viscosity. The change in $\alpha$ (cf. Eq. 4) exerted a profound impact on the expanding
rate but appears to have similar final bubble sizes. A rise in $n$ (cf. Eq. 3) retarded the
growth but enhanced the shrinkage. The model by Fan et al. [171], however, didn’t
take into account the effects of limitations imposed by the diffusion of water, and
bubble coalescence and rupture. A more compressive dynamics model was later
developed by Alavi et al. [174,175] for sc-CO2 extrusion and post-extrusion processing of starchy extrudates.

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

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

6.3. Rheology-film blowing property relationship

Generally, a high extensional viscosity is favourable for film blowing since it increases take-up force which enhances bubble stability. It has been established that higher extensional viscosity can be obtained by the increase of molecular weight and the generation of strain hardening [165]. In addition, strain hardening is also
favourable for the homogeneity of film thickness [165]. This is also true for starch polymers as reported by Zullo and Iannace [160]. Thunwall et al. [96] investigated the relationships between the processing parameters (glycerol content, moisture content, and temperature) that influence the shear viscosity and the film blowing properties of TPS. It has been showed that, when the shear viscosity is higher than a critical value, TPS become too stiff to expand during the blowing and the material fails in a brittle manner at the calendering nip. Moreover, the significant increase in the torque required from the extruder and the die pressure as a result of high viscosity also makes the film blowing process difficult [96]. In contrast, when the viscosity is too low, the surface of the extruded material become sticky, resulting in a double-walled film impossible to separate through the calendering nip. A low viscosity accompanied by high temperature and high plasticiser content might also cause the bubble formation in the extrudate, and the subsequent rupture of the stretched melt [96]. These relationships are illustrated in [Fig. 13].

[Insert Fig. 13 here]

6.4. Other rheology-processing/product property relationships

In extrusion processing, a higher viscosity may result in enhanced thermomechanical treatment (SME = Γ × N/Q) within the extruder barrel, which may cause a greater degree of molecular degradation which could deteriorate the mechanical properties of final products [58,84,108,113,127,130]. In injection moulding with a given back-pressure, a lower melt viscosity can result in a higher backward flow rate and thus a longer refill time (a lower net flow rate) [181]; besides,
the adhesion of TPS part to the mould can occur at low viscosity (though the adhesion can be minimised by using an appropriate lubricant) [45]. In various kinds of processing, viscosity can affect the mechanical properties since it has a relationship with blend compatibility and morphology as already discussed in Section 6.1. Furthermore, it can be expected that an appropriate viscosity is important for the orientation process of TPS products which would improve the mechanical properties [144,182].

7. Summary

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

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

8. Future perspectives

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

1) Viscoelastic properties and extensional viscosity

As discussed in Section 5.2, during processing, shear viscosity may not be sufficient to characterise the rheology of starch polymers. Starch polymer melts can display strong melt elastic properties, which relates to the processing and product quality. Also many processing flows are mixed flow – both shear and extensional flows – and thus extensional viscosity measurements are also vital. New techniques need to be developed for the more accurate characterisation of the elasticity of starch polymer melts. Much work needs to be done to establish the relationships between formulation and processing conditions, and melt viscoelastic properties and extensional viscosity. It is also worth to carry out research to link the melt elastic properties to product properties of starch polymers. Regarding this, strain hardening
behaviour which can be related to processes such as foaming and film blowing should be a focus.

2) “Complete” modelling

The changes in starch under processing are not only affected by temperature, plasticiser, and SME, but also are affected by thermal energy input and pressure. Additionally, there is currently no simple relationship between starch granular transformation and macromolecular degradation, and melt viscosity. It has been shown that, under thermomechanical treatment, the viscosity of starch with low content of plasticiser first increases and then decreases to a nearly stable value [31,32]. As a result, the processing-structure-rheology relationship needs to be carefully examined. Furthermore, it is meaningful to differentiate the effects of temperature and plasticiser on starch microstructural changes (which subsequently impact the rheology) from those affects directly on the rheology.

Different parameters (temperature, plasticiser content, SME, etc.) in current empirical models actually interacts with each other, which has to be considered into future modelling work. More importantly, the rheology of starch as a polymer depends on not only temperature and plasticiser content, but also structural factors such as molecular weight, polydispersity, conformation, and composition. Rheological modelling should consider these structural factors and based on structural models (e.g. the hard sphere suspension model), enabling the linkage between rheology and polymer physics and chemistry. In this way we are moving toward the development of a “complete” constitutive rheological model for starch polymeric materials.
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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 \( \eta / a_{T,MC,GC} \) as a function of \( \gamma \cdot a_{T,MC,GC} \) where \( a_{T,MC,GC} \) is the shift factor defined as:

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

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 amylomaize 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).

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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.
L = 200 mm
W = 30 mm

Fig. 5 – Xie et al.
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.
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.

<table>
<thead>
<tr>
<th>Starch</th>
<th>Amylose content (%)</th>
<th>V-type polymorph (%)</th>
<th>Double-helix (%)</th>
<th>Amorphous (%)</th>
<th>Degree of crystallinity (%)</th>
<th>XRD pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waxy maize</td>
<td>3.4</td>
<td>0</td>
<td>47</td>
<td>53</td>
<td>29</td>
<td>A</td>
</tr>
<tr>
<td>Regular maize</td>
<td>24.4</td>
<td>3</td>
<td>33</td>
<td>64</td>
<td>21</td>
<td>A</td>
</tr>
<tr>
<td>Amylomaize (Gelose 50)</td>
<td>56.3</td>
<td>7</td>
<td>18</td>
<td>75</td>
<td>13</td>
<td>B</td>
</tr>
<tr>
<td>Amylomaize (Gelose 80)</td>
<td>82.9</td>
<td>14</td>
<td>38</td>
<td>68</td>
<td>15</td>
<td>B</td>
</tr>
</tbody>
</table>

*aThe maximum error for amylose content determination was 6%. bThe maximum standard deviation for the $^{13}$C NMR analysis calculation was 2.4%. cThe maximum error for the calculation of degree of crystallinity was 3.5%.
<table>
<thead>
<tr>
<th>Type</th>
<th>Rheometer</th>
<th>Shear rate variation method</th>
<th>Measurement type</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Shear rate (s⁻¹) / frequency (rad/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off-line</td>
<td>Rotational</td>
<td>Rotation speed</td>
<td>Viscoelasticity</td>
<td>Small amount of sample</td>
<td>Serious loss of water; insufficient SME input for melting starch</td>
<td>10²–10³</td>
<td>[88]</td>
</tr>
<tr>
<td>Plunger-type</td>
<td>Plunger slit/capillary</td>
<td>moving speed</td>
<td>Steady shear viscosity</td>
<td>Small amount of sample; easy to use; for pre-shearing rheometer (Rheoplast), the processing conditions are independently controlled.</td>
<td>Insufficient SME input for melting starch; minor loss of water and unstable results (pre-shearing rheometer)</td>
<td>10⁻¹–10³</td>
<td>[45, 47, 51, 83, 93, 94, 97, 99, 100, 101, 103, 160, 162]</td>
</tr>
<tr>
<td>Extruder-type</td>
<td>Screw speed slit/capillary</td>
<td>Screw speed</td>
<td>Steady shear viscosity; extensional viscosity; first normal stress difference</td>
<td>Multi-step extrusion processing and post processing conditioning allowed</td>
<td>Subsequent degradation</td>
<td>10¹–10³</td>
<td>[52, 54, 65, 105, 107, 108]</td>
</tr>
<tr>
<td>In-line</td>
<td>SSE +</td>
<td>Screw speed</td>
<td>Steady shear viscosity; extensional viscosity; first normal stress difference</td>
<td>Approximate the practical extrusion process</td>
<td>Change in thermomechanical history</td>
<td>$10^{9.1-10^4}$</td>
<td>[2, 48, 53, 84, 113]</td>
</tr>
<tr>
<td>---------</td>
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<td>-------------------------------------------------</td>
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</tr>
<tr>
<td>CDV/SDV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSE +</td>
<td>Feeding rate</td>
<td>Steady shear viscosity; extensional viscosity; first normal stress difference</td>
<td>Approximate the practical extrusion process</td>
<td>Change in thermomechanical history</td>
<td>$10^{1.4}$</td>
<td>[93, 110, 112, 117]</td>
<td></td>
</tr>
<tr>
<td>CDV/SDV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSE/TSE +</td>
<td>Die channel flow</td>
<td>Steady shear viscosity; extensional viscosity; first normal stress difference</td>
<td>Approximate the practical extrusion process; no/little change in thermomechanical history</td>
<td>–</td>
<td>$10^{9.3}$</td>
<td>[77, 78, 85, 119, 120, 130, 131]</td>
<td></td>
</tr>
<tr>
<td>DCD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>Multipass</td>
<td>Piston moving speed</td>
<td>Steady shear viscosity</td>
<td>Small amount of sample; no loss of water</td>
<td>Steady rheological state is required.</td>
<td>$10^{1.1-10}$</td>
<td>[135]</td>
</tr>
<tr>
<td>Mixer-type</td>
<td>Rotor speed</td>
<td>Steady shear viscosity.</td>
<td>Small amount of sample</td>
<td>Minor loss of water; shear stress and shear rate are approximately calculated; steady rheological state is required.</td>
<td>$10^{9.3}$</td>
<td>[137]</td>
<td></td>
</tr>
</tbody>
</table>
SSE: single-screw extruder; TSE: twin-screw extruder; CDV: capillary/cylindrical die viscometer; SDV: slit die viscometer; DCD: double-channel die.

*According to the published results in the literature*
Tab. 3 Summary of the different shear viscosity power-law models used in the literature

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

78.5; $n = 0.51$

36.0; $n = 0.36$

0.49; $n = 0.68$
<table>
<thead>
<tr>
<th>Authors</th>
<th>Material</th>
<th>Method</th>
<th>Temperature</th>
<th>Moisture Content</th>
<th>Dynamic Viscosity</th>
<th>Logarithmic Temperature Coefficient</th>
<th>Logarithmic Shear Rate Coefficient</th>
<th>Other Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vergnes and Villemaire, 1987 [100]</td>
<td>Maize starch</td>
<td>Pre-shearing</td>
<td>110–170</td>
<td>21–33 (w.b.)</td>
<td>$10^3$</td>
<td>$K = K_0 \exp[\frac{E}{RT} - \frac{1}{T_0}]$</td>
<td>$\Delta E/RT = 4250; \alpha = 10.6; \beta = 0.088; K_0 = 7.36; \alpha_1 = 6.59 \times 10^{-4}; \alpha_2 = 1.12 \times 10^{-1}; \alpha_12 = 7.28 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Senouci and Smith, 1988 [93]</td>
<td>Maize grits</td>
<td>In-line</td>
<td>100–140</td>
<td>20.1–31.5 (w.b.)</td>
<td>$10^3$</td>
<td>$K = K_0 N^\frac{\alpha}{RT} \exp(-\alpha MC)$</td>
<td>$E/IR = 2834; \alpha = 0.032; k = 0.541; K_0 = 21.5; n = 0.75$</td>
<td></td>
</tr>
<tr>
<td>Lai and Kokini, 1990 [113]</td>
<td>Waxy maize starch</td>
<td>In-line</td>
<td>100–150</td>
<td>20–40 (w.b.)</td>
<td>$10^3$</td>
<td>$K = K_0 \exp\left[\frac{(E + E'MC)}{RT} - \frac{1}{T_0} - \frac{\alpha MC}{(\alpha + \alpha'T) MC} \right]$</td>
<td>$E/IR = 50168; E'/IR = -3159; \alpha = 11.502; \alpha' = -0.0093; k = 0.056; K_0 = -112.45; n = 0.312$</td>
<td></td>
</tr>
<tr>
<td>Wang et al., 1990 [117]</td>
<td>Wheat flour</td>
<td>In-line</td>
<td>169–187</td>
<td>18–24 (w.b.)</td>
<td>$10^3$</td>
<td>$K = K_0 \exp[-\alpha MC] (1-\beta W)$</td>
<td>$\alpha = 8.71; \beta = 9.8 \times 10^{-4}; K_0 = 3.62 \times 10^{-5}; n = 0.15$</td>
<td></td>
</tr>
<tr>
<td>Author(s)</td>
<td>Material</td>
<td>Process Type</td>
<td>Temperature Range</td>
<td>MC Range</td>
<td>Activation Energy</td>
<td>Specific Heat Capacity</td>
<td>Parameters</td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>Padmanabhan et al.</td>
<td>Maize meal</td>
<td>In-line</td>
<td>150–180</td>
<td>MC: 25–45</td>
<td>$10^{2} - 10^{3}$</td>
<td>$K = K_0 \exp (E/RT - \alpha MC)$</td>
<td>$E/R = 2726 \text{ K}; \alpha = 1.99; k = 3.5 \times 10^{-8}; K_0 = 249; n = 0.28$</td>
<td></td>
</tr>
<tr>
<td>Padmanabhan et al.</td>
<td>Maize meal</td>
<td>In-line</td>
<td>160–180</td>
<td>MC: 25–35</td>
<td>$10^{1} - 10^{3}$</td>
<td>$K = K_0 \exp (E/RT - \alpha MC)$</td>
<td>$E/R = 2451; \alpha = 4.63; K_0 = 106.25; n = 0.37$</td>
<td></td>
</tr>
<tr>
<td>Della Valle et al.</td>
<td>Potato starch</td>
<td>In-line</td>
<td>139–176</td>
<td>MC: 26–32</td>
<td>$10^{1} - 10^{3}$</td>
<td>$K = K_0 \exp [E/RT(1/T - 1/T_0) - \Delta E/RT]$</td>
<td>$\Delta E/RT = 5710; \alpha = 9.45; \beta = 0.997; \alpha_2 = -60.6; \alpha_3 = -0.44; \alpha_{12} = 0.418; \alpha_{13} = -0.0341; \alpha_{13} = 2.1 \times 10^{-4}; \alpha_{23} = -0.0341; \alpha_{13} = -2.1 \times 10^{-4}; n_0 = 14.33$</td>
<td></td>
</tr>
<tr>
<td>Wang et al.</td>
<td>Maize starch-PVA</td>
<td>Offline (PCR)</td>
<td>100–120</td>
<td>MC: 26–45</td>
<td>$10^{1} - 10^{4}$</td>
<td>$K = K_0 \exp (E/RT - \alpha MC)$</td>
<td>$E/R = 6332.5; \alpha = 6.1; K_0 = 1.391 \times 10^{-2}; n = 0.31$</td>
<td></td>
</tr>
<tr>
<td>Authors</td>
<td>Sample Type</td>
<td>Methodology</td>
<td>Temperature Range</td>
<td>Moisture</td>
<td>Stress</td>
<td>Activation Energy</td>
<td>Pre-exponential Factor</td>
<td>Activation Energy</td>
</tr>
<tr>
<td>------------------</td>
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</tr>
<tr>
<td>Willett et al.,</td>
<td>Maize starch</td>
<td>Offline</td>
<td>110–180</td>
<td>MC: 15–30</td>
<td>–</td>
<td>$10^3$</td>
<td>$K_0 \exp(E/RT - aMC)$</td>
<td>$E/RT = 8500$; $\alpha = 12.6$; $K_0$ and $n$ not determined.</td>
</tr>
<tr>
<td>1995 [108]</td>
<td></td>
<td>(SSE+CDV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Della Valle et</td>
<td>Maize starch (23%</td>
<td>In-line</td>
<td>130–160</td>
<td>MC: 20.5–</td>
<td>–</td>
<td>$10^3$</td>
<td>$K_0 \exp(E/RT - aMC - \beta SME)$</td>
<td>$E/IR = 6140$; $\alpha = 18.6$; $\beta =$</td>
</tr>
<tr>
<td>al., 1996 [127]</td>
<td>amylose content</td>
<td>(TSE+Rheopa)</td>
<td>36.0 (w.b.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ilo et al.,</td>
<td>Maize grits</td>
<td>In-line</td>
<td>150–160</td>
<td>MC: 13–17</td>
<td>–</td>
<td>(Not given)</td>
<td>$K_0 \exp(E/RT - aMC)$</td>
<td>$E/IR = 18441$; $\alpha = 0.097$; $K_0$ and $n$ not determined.</td>
</tr>
<tr>
<td>1996 [110]</td>
<td></td>
<td>(TSE+CDV)</td>
<td>(w.b.)</td>
<td></td>
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<tr>
<td>Aichholzer and</td>
<td>(Starch type not</td>
<td>Off-line</td>
<td>70–110</td>
<td>MC: 12.5</td>
<td>Sample ageing</td>
<td>$10^4$</td>
<td>$K_0 \exp(1/R[(g_1 + g_2GC)(1/T_0 - 1/T) + (t_1 + t_2T)(1/GC_0 - 1/GC)])$</td>
<td>$g_1 = -1.47 \times 10^3$; $g_2 = 1.62 \times 10^3$; $t_1 = 6.45 \times 10^3$; $t_2 = -1.20 \times 10^3$; $K_0$ and $n$ not determined.</td>
</tr>
<tr>
<td>Fritz, 1998 [106]</td>
<td>(SSE+piston+SDV)</td>
<td></td>
<td></td>
<td>GC: 15–25</td>
<td>and screw shear</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Authors</td>
<td>Type</td>
<td>Methodology</td>
<td>MC Range</td>
<td>Properties</td>
<td>Equation</td>
<td>Parameters</td>
<td></td>
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<tr>
<td>Brouillet et al., 2002</td>
<td>Maize flour</td>
<td>Mixer</td>
<td>89–115 (w.b.)</td>
<td>steady molecular and rheological state was achieved before measurements.</td>
<td>$K = K_0 \exp(E/RT - \alpha MC)$</td>
<td>$E/R = 3090; \alpha = 10.64; K_0 = 566; n = 0.23$</td>
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<tr>
<td>Martin et al., 2003 [84]</td>
<td>Wheat starch</td>
<td>In-line (SSE+CDV; SSE+SDV)</td>
<td>110–150 (w.b.)</td>
<td>the use of both CDV and SDV ensured a wide shear rate range.</td>
<td>$K = K_0 \exp(E/RT - \alpha MC - \alpha'GC - \beta SME)$</td>
<td>$E/R = 5860; \alpha = 10.9; \alpha' = 4.7; \beta = 5.9 \times 10^{-3}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Berzin et al., 2007 [129]</td>
<td>Wheat starch</td>
<td>Inline (TSE+DCD)</td>
<td>73–113 (w.b.)</td>
<td>–</td>
<td>$K = K_0 \exp[n(E/R(1/T - 1/T_0)] - \alpha(MC - MC_0) - \beta(SME - SME_0)]$</td>
<td>$E/R = 5150; \alpha = 10.91; \beta = 0.0028; K_0 = 1920; n = 0.53; T_0 = 363 K; MC_0 = 0.4; SME_0 = 325$</td>
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<tr>
<td>Della Valle et al., 2007 [103]</td>
<td>Wheat starch</td>
<td>Pre-shearing</td>
<td>95–155 (w.b.)</td>
<td>–</td>
<td>$K = K_0 \exp[n(E/R(1/T - 1/T_0)] - \alpha'(GC - GC_0)]$</td>
<td>$E/R = 14530; \alpha' = 25.1; K_0 = 8080; n = 0.28; T_0 = 498; MC_0 = 0.27$</td>
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<tr>
<td>Sandoval and Barreiro [99]</td>
<td>Maize starch</td>
<td>Off-line</td>
<td>85–120</td>
<td>MC: 27–37</td>
<td>Starch was processed in the Off-line (Plunger-type capillary) rheometer.</td>
<td>$K = K_0 \exp(E/RT - aMC)$</td>
<td>$E/R = 1435; \alpha = 0.05072; K_0 = 12.06; n = 0.16$</td>
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<tr>
<td>Tajuddin et al. 2011 [135]</td>
<td>Waxy maize starch</td>
<td>MPR</td>
<td>90–130</td>
<td>MC: 28–44</td>
<td>Steady molecular and rheological state was achieved before measurements.</td>
<td>$K = K_0 \exp(E/RT - aMC - a'GC)$</td>
<td>$E/R = 7396; \alpha = 17.15; \alpha' = 5.564; K_0 = 0.03073; a_1 = 0.03180; a_2 = 20.09; a_3 = 0.04444; a_4 = 0.09083; a_5 = 70.84; n_0 = 13.03$</td>
<td></td>
</tr>
</tbody>
</table>

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 (Pa·s$^n$); $E/R$: reduced flow activation energy (K); $T$: temperature (K); MC: moisture content; GC: glycerol content; SME: specific mechanical energy (kWh·t$^{-1}$); W: mechanical energy ($\times 10^8$ 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. Reproduced with permission.

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

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