

**FLOW BEHAVIOUR AND VISCOELASTICITY OF
POLYPROPYLENE-KAOLIN COMPOSITES**

by

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LIST OF SYMBOLS

T_g	Glass transition temperature
$\dot{\gamma}_w$	True wall shear rate
$\dot{\gamma}$	Shear rate
$\dot{\gamma}_{app}$	Apparent shear rate
τ_w	True wall shear stress
τ	Shear stress
τ	True shear stress
η_{app}	Apparent Viscosity
η	Viscosity
η_0	Zero-shear viscosity
η_{sp}	Specific viscosity
η_{int}	Intrinsic viscosity
η_{red}	Viscosity number
σ_{ij}	Stress tensor
N_1	First normal stress
N_2	Second normal stress
M_v	Molar Mass
Q	Volume flow rate

LIST OF ABBREVIATIONS

CAD	Computer Aided Drawing
CAE	Computer Aided Engineering
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MFI	Melt Flow Index
PP	Polypropylene
PPgMA	Maleic Anhydride- <i>graft</i> -Polypropylene
PS	Polystyrene
PVT	Pressure-Volume-Temperature
SEM	Scanning Electron Microscopy
wt%	Weight Percentage
vs.	Versus

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FLOW BEHAVIOUR AND VISCOELASTICITY OF POLYPROPYLENE-KAOLIN COMPOSITES

ABSTRACT

Melt flow and viscoelastic behaviour of polypropylene kaolin (PP-kaolin) composites were investigated using a single screw extruder at various filler loading, temperature, extrusion cycle and die diameter. It was discovered that for the effect of filler loading, 5 wt% of kaolin loading has caused MFI value and apparent viscosity of the composites to be slightly reduced with respect to pure PP. Whereas, above 5 wt% of kaolin loading the apparent viscosity started to increase. Experimental results also showed that swelling ratio and MFI decreased gradually with increasing amount of filler loading but unexpectedly at 30wt% of kaolin loading, the swelling ratio started to increase proportionately with shear rate. This was attributed to the void formation in between the cross-sectional area of the extrudates. Meanwhile, investigation for the effect of temperature, has proven that MFI increased while apparent viscosity and swelling ratio are reduced with temperature increment. It was also observed that a decrease in processing temperatures may caused significant bubble-like surface morphology. In the degradation studies, the results indicated that increase in processing temperature led to molecular chain scission of the polymer segment. However, a reverse trend of results was detected for the effect of extrusion cycle which indicated that the polymer chain segment are more prone to crosslink rather than chain scission with increasing number of extrusion cycles. Meanwhile for the determination of the true viscosity using different die geometry, it was found that the true viscosity is lower than the apparent viscosity after the Bagley and Rabinowitsch

corrections were done. Later using the obtained apparent and generated true viscosity data, a cadmould[®] simulation was performed on a Computer Aided Simulation (CAD) dumbbell model to determine the filling and shear stress analysis. The results has showed that, high-viscosity apparent viscosity data has substantially reduce the mould filling temperature, pressure, melt shear stress and increase the melt velocity during mould filling due extra heat generation from viscous dissipation effect compared to the true viscosity data.

SIFAT ALIRAN DAN KELIKATKENYALAN KOMPOSIT POLIPROPILENA-KAOLIN

ABSTRAK

Sifat aliran leburan dan kelikatkenyalan komposit polipropilena-kaolin (PP-kaolin) telah dikaji dengan menggunakan mesin pengestrudan skru tunggal untuk kandungan pengisi, suhu, kitaran pengestrudan dan geometri dai diameter yang berbeza. Secara amnya, untuk kesan kandungan pengisi, didapati bahawa pada 5wt% kandungan kaolin, nilai MFI dan kelikatan ketara komposit sedikit menurun berbanding PP sebenar. Sementara itu melebihi 5wt% kandungan kaolin, kelikatan ketara mula meningkat. Di samping itu, nisbah pembengkakan dan MFI menurun dengan perlahan dengan pertambahan kandungan pengisi, tetapi tanpa dijangka pada kandungan kaolin 30wt%, nisbah pembengkakan mula meningkat berkadar langsung dengan tegasan ricih. Hal ini adalah berkaitan dengan pembentukan lohong kosong di bahagian keratan rentas hasil pengestrudan. Manakala, untuk kesan suhu pula, ia telah dibuktikan bahawa nilai MFI telah meningkat. Kelikatan ketara dan nisbah pembengkakan pula menurun dengan peningkatan suhu. Selain itu dengan pengurangan suhu pemprosesan, morfologi permukaan ekstrudat menghasilkan gelembung yang lebih besar berbanding pada suhu pemprosesan yang lebih tinggi. Manakala untuk kajian degradasi pula, didapati bahawa peningkatan suhu pemprosesan akan menyebabkan proses pengguntingan rantai terhadap segmen polimer. Walau bagaimanapun, kitaran pengestrudan terhadap degradasi menunjukkan data yang sebaliknya diperolehi iaitu tindakbalas sambung-silang antara rantaian adalah lebih ketara dengan peningkatan kitaran pengestrudan. Manakala untuk

kajian terhadap penentuan kelikatan sebenar dengan menggunakan geometri dai yang berbeza pula menunjukkan kelikatan sebenar adalah lebih rendah berbanding kelikatan ketara selepas pembetulan Bagley dan Rabinowitsch dijalankan. Kemudiannya data kelikatan ketara yang diperolehi dan kelikatan sebenar yang dijana akan digunakan dalam program simulasi Cadmould[®] ke atas model CAD *dumbell* untuk menentukan analisa pengisian dan tegasan ricih. Keputusan menunjukkan bahawa kelikatan ketara yang mempunyai kelikatan yang lebih tinggi telah merendahkan suhu acuan pengisian, tekanan, tegasan ricih dan meningkatkan kelajuan aliran semasa proses pengisian acuan disebabkan oleh hasilan haba yang berlebihan semasa proses pengisian acuan berbanding dengan data kelikatan sebenar.

CHAPTER 1

INTRODUCTION

1.1 Research Background

During the past decade, development of filled polymer composites has generated intensive activities in polymer technology field with regards to significant commercial importance due to wide variety of applications such found in automotives industries, electric and electronics as well as for building structural application. In order to tailor product characteristics and to meet customer requirements, it is often necessary to change physical properties of polymer compound and in this case the utilization of, particulate-additives in reducing the production cost of molded product. Although cost reduction plays an important role, compromise between the physical and mechanical properties such as stiffness, hardness, high temperature creep resistance, flexural strength, etc also need to be taken into consideration. One of these particulate additives is fillers which are defined as additives in solid form that is incorporated in a polymer matrix.

Active filler provide specific mechanical or physical properties improvement thus also known as reinforcing fillers whereas inert fillers or extender are used to increase the volume of the compounded polymer and lower the compounded polymer price. Studies of inorganic origin mineral fillers such as talc, kaolin, mica, CaCO_3 , silica, silicates, glass beads and fibers are relatively common and there have been many researches done extensively throughout the years (Leong et al., 2004; Ariffin et al., 2008; White and Suh, 2006).

Talc, mica and kaolin are used to enhance the stiffness and strength of the filled plastics. While, CaCO₃-filled grades are reported to improve impact strength. Fibrous fillers usually provide good tensile strength. Mechanical characteristics of these fillers are dominantly influenced by their interfacial interactions, which depend on the extent of the interfacial interaction. High surface area fillers may give more surface contact between filler and matrix, thus increasing properties of the composites. Meaning, the finer the particle size, the higher the contact surface area is available. However, finer particles are exposed to a greater tendency of agglomeration, consequently leading to an adverse effect on rheological properties as well as the end product properties.

According to Eberle et al. (2008), the addition of fiber will create a dramatic effect on both shear and shear-free flow rheological behavior of a fluid. The fiber orientation distributions will initially impart the mechanical properties of the produced composites. On the other hand, Lee and Han (2003) has pointed out that the melt viscosity of polymer matrix plays an important role in dispersing the organoclay aggregates to secure the polymer matrix compatibility along with its connections to the tensile properties.

Several factors will govern the end properties of particulate-filled polymers such as the component properties (matrix and filler), composition and structure. Largely, the effect of fillers structure usually depends greatly on their shape, particle size and particle size distribution. It has been known that, higher loading of filler will significantly increase shear viscosity of polymer matrix since fillers will obstruct plastic to flow. Depending on its structure, adverse results might be observed. Previously, it has been found that, talc particles are able to slide against each other during application of shear forces due to its

platy shape which consequently promote a slight decrease in the plastic flow with respect to pure matrix alone (Suh and White, 2006).

Besides filler loading, the processing temperatures play a vital role in processing polymer composites. However, commercial polymer processing involves extremely large rates of temperature change before they are turned into final product. Usually, polymers are processed above their glass transition temperature (T_g) in order for the polymer molecule to have enough thermal energy to become mobile and past other polymer molecules where there is ample free volume available. Higher processing temperature promotes easy processing due to increase in melt flow. In plastic industries, extrusion is a primary utilized processing technique and practically all commercial polymeric materials are extruded at least once during their life cycle. Although high temperature will provoke melt flow during extrusion process but in contrast it will affect thermal stability of polymeric materials (Brydson, 1989).

Moreover intensive shear rates and extensional flows will results in variations of product performance which can be contributed by polymer degradation thus leading to unwanted surface appearance and inferior performance. Depending on the type of polymeric materials, increasing the processing temperature will trigger to different mechanisms of degradation reactions. Usually degradation may leads to chains scissions and transfer reaction which initially result in lowering the molecular weight and change in product physical appearance.

Besides the effect of temperature, melt viscosity of the polymer composites will substantially increase with incorporation of filler and reduce its elasticity as the amount of filler increases. On the contrary, the elasticity reduces as the temperature increases. The elastic effect is demonstrated by the polymer chain segment recovery after the shear is removed. It is the most important characteristic that explains the die swell phenomenon where the extruded polymer appears to be larger than that of the orifice.

Many studies have been done to determine filler polymer elastic behavior at various processing parameters previously. Ariffin et al. (2008) has dedicated partially of their work on extrudate swell of treated calcium carbonate and talc-filled polypropylene. They proved that increase in temperature will cause reduction in swelling ratio, while at higher temperature, the swelling ratio starts to decrease with increasing shear rate due to better filler dispersion. Moreover, Liang et al. (2000) who has investigated the swell behavior of glass bead-filled low-density polyethylene composites claims that, die swell increased non linearly with increasing wall true wall shear rate ($\dot{\gamma}_w$) for LDPE/3000 treated bead, while the die swell remains almost constant when ($\dot{\gamma}_w$) for LDPE/3000U untreated glass bead is greater than 2000 s^{-1} at a constant temperature.

Another common effect that is caused by elastic component present in the polymer melt is flow instabilities. Once the extrudate exits the die, the melt flow struggles to return to its original position as high stress is removed. Due to viscoelastic nature of polymers, the extrudate flowing out of the die manifests its elastic portion in many ways such as die swell and sometimes exhibiting flow instabilities. Again Ariffin and his coworkers (2006)

further their research in observing the melt fracture of the multicomponent composites and proposed that the compound with the highest die swell ratio exhibit the most severe melt fracture. Besides melt fracture defect, Hristov and Vlachopoulos (2007) have reported that, higher shear rate is beneficial for the production for smoother extrudate of wood polymer composites whereas severe extrudate tearing and surface roughness were observed in a case of 2 mm die diameter with respect to 1 mm die diameter.

Based on the relationship between processing variables and its significant effect on mechanical properties, it needs extensive knowledge in rheological studies and proper research. Besides extrusion, injection molding is a very important processing technique to turn the polymer melt into desired final shape. To fabricate a low cost polymer mould and to avoid a lot of time on trial and error method in the early stage of manufacturing new product design, designers have utilized computer aided engineering (CAE) software to evaluate injection moulding flow analysis in predicting stress area and overcome flow problems. Currently, there are several CAE softwares for injection molding available in the market and examples of these software are Moldflow[®], Cadmould[®] and Moldex3D[®].

In order to make a successful and meaningful simulations, rheological data such as PVT (Pressure-Volume-Temperature), thermal properties and others parameter are required to give input for accurate simulations result in comparison to the actual plastic processing conditions. Nonetheless, other major advantage is that the software is capable of estimating the development of new composites mechanical properties provided sufficient rheological data are available. Previously, Rahman et al. (2008), has made an

effort to study the injection moulding flow analysis using the Mouldflow® simulation software for natural fiber composites window frame and has proven that, it is able to simulate the moulded composites article but improvisation has to be made on the rheological data use.

1.2 Problem Statement and Research Approach.

Although extensive research has been carried out to determine the rheological behavior of mineral filler filled composites, they are different results reported by various researchers. One might agree with one claim while other express disagreement and their analysis is often still under debate. Besides focusing on the processing variables use, type of filler introduce, amount of filler loading, filler structure and etc, filler treatment has captured numerous attention by the scientist to improve the rheological and elastic properties.

Many researchers have implemented and dedicated their research on polypropylene (PP) filled with kaolin as filler in forming polymer composite especially in Malaysia since it has been proven that kaolin can function as reinforcing fillers (Leong et al., 2004; Ariffin et al., 2008; Maiti¹ et al., 2003). The main objective of their research is to determine the physical, mechanical and rheological properties provided by kaolin in order to replace talc which readily available in the market. Similar to talc, kaolin plate-like structure provide improvement in rigidity depending on the filler aspect ratio and it is also discovered that kaolin is able to become a “toughening agent” that improvises higher impact strength to polymer composites. It has been reported by Leong et al. (2004) that the

enhancement of flexural properties is attributed to higher aspect ratio and particle orientation of kaolin.

However, talc proves to be slightly better than kaolin. This could be pointed to kaolin small particle size which would impose higher surface energy together with the presence of a polar group that contribute to particles agglomeration and this result in the reduction of surface interaction between PP and kaolin. Hence, the scenario presents significant difficulties in particles dispersion during processing which will eventually give rise to nonuniformity of end properties. Since then, various attempts to improve the filler dispersion have been made which subsequently affect the rheological behavior of the composites.

Maiti² et al. (2003) claimed that the introduction of modified agent which is LICA 38, has obviously modified the rheological properties of PP kaolin composites and enhance the bonding between PP and kaolin. Meanwhile, Ariffin et al. (2006) found that PPgMa treated kaolin-filled composites promote processing enhancement and provoke dispersion homogeneity of the composites. Based on both studies, it is noted that it is necessary to incorporate coupling agent inside PP since PP macromolecules do not have polar groups to interact physically or chemically with the mineral fillers.

Correlated with the results obtained by previous researches, the efforts are made to further investigate the viscoelastic behaviour of the PP-kaolin composites. A stand-alone single screw extruder is utilized in measuring the flow properties and composites rheological behaviour. The data collected throughout the studies, will then utilized for

simulations studies using the CadMould® software. The attempt of this study is to understand the bridging between the rheological data obtained and its correlations with the flow and viscoelastic behavior of PP-kaolin composites. Besides, the obtained rheological data will also provide useful information and accurate prediction on composite flow and end properties.

1.3 Objectives

The investigation of flow behavior and viscoelasticity of PP-Kaolin composites are covered in this research. The effort has been made to analyze and optimize processing variables throughout the extrusion process. Obviously, there are five main objectives targeted which are listed as follows:

- 1) To study the effect of kaolin loading towards flow and elastic behavior of PP-kaolin composites. The important of this study is to determine the maximum capacity of kaolin loading capable of providing optimum process ability that could provide a non-defect criteria to the extrudate.
- 2) Besides filler loading, the effect of processing temperature is also investigated. Different die temperatures ranging from 190°C to 230°C are utilized during extrusion process and at various temperatures, the flow and elastic behavior of a polymer are projected to behave differently. The study on temperature will provide useful information on the rheological behavior of the composites.

- 3) The studies on flow and elastic behavior of recycle composites passing the extruder several times are also carried out. The relevant of this study is to determine the ability of the material to withstand thermal and mechanical mechanism which could lead to molecular degradation.
- 4) The effect of different flow geometries, i.e. die diameter, on the flow and elastic behaviors are also investigated. The data generated are used to perform Bagley correction procedure that provides the excess pressure value presence due to the ends effect.
- 5) The last objectives is to utilize the obtained rheological data in Cadmould® software and perform simulation process on a dumbbell CAD model to determine possible flow profile that would be generated during mould filling. The simulation was carried out at the temperature of 210°C.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Rheology

Several billion tonnes of polymers are annually used to make commercial products for worldwide consumption and recently the usage of these materials have become very important in our daily life. Normally, polymer is used to fulfill consumer commodity needs. But in this era of globalization, polymer has been utilized for engineering and specialty application purposes such as in automotive industries, electric and electronics field and in some occasions, structural application. Before these materials are turned into their final forms, most are brought to their liquid states for processing and this pronounces the importance of studying their rheological behaviour.

Rheology can be defined as the science of flow and deformation (Gupta, 2000; Carreau et al., 1997). While, viscosity can be defined as a measurement of internal resistance to shearing stress or extensional stress imposed by a fluid element to the resulting applied shear rate. Both subjects are very important for polymers and polymeric composites because flow is always involved in the processing and fabrication of such materials in order to transform them into useful objects.

For low molecular weight polymer fluid, the study of rheology involves the measurement of viscosity. For such polymer fluid, the viscosity depends primarily upon temperature and hydrostatic pressure. However, the rheology of high molecular weight

polymer liquid whether neat or filled, is much more complex because polymeric fluids show non-ideal behavior and it is a material with viscoelastic nature (Gupta, 2000). Polymer melts are not simple Newtonian fluids but rather relaxation liquids in which the rheological data depend on the experimental observation time (or measured frequency) and temperature (Hsich, 1982). The materials flow properties cannot be described by a single constant viscosity.

Brydson (1970) proposed two common explanations for polymeric system which represent polymer solutions and polymer melts respectively;

- a) In polymer solution, highly solvated molecules or particles may be present in a polymer solution. As the shear rate increases, the solvated layers may be sheared away resulting in decreased interaction of the particles (because of their smaller effective size) and consequently reduction in apparent viscosity occurs. Moreover, increase in free volume due to increasing dilution (or decrease in polymer concentration) may also affect the mobility of polymer molecules in a polymer solution.
- b) In polymer melt, asymmetric molecules or particle are extensively entangled and/or randomly oriented at rest. These entanglement and random-coil configuration give restrictions towards flow at low shear rate. Increasing temperature will increase the free volume of the polymer systems, which in turn gives better polymer molecules mobility. At high shear rate and temperature, the restrictions are overcome where entanglements are disentangled leading to reduction in viscosity of the melt dramatically.

Research scope of polymer rheology can be divided into two different approaches, depending on convenience and the effectiveness of applications. Firstly is a scientific approach, where a study and modeling the structural relaxation spectrum of polymers in a prerequisite of understanding polymer rheology. The structural relation provide detail on understanding the glass and rubber transition and therefore in predicting structure-property relationships of polymer materials. The model of structural relation spectrum will give a physical insight for comprehension and prediction of dynamic mechanical properties, thermal stress, fracture mechanics, fatigue, yield stress, heat transfer and adhesion of polymeric materials. Secondly followed by an engineering approach where the understanding in scientific approach is applied in the application of polymer processing (Hsich, 1982).

Better understanding of the rheological properties could offer some help in determining molecular weight and molecular weight distribution of a polymer in order to provide optimum processing condition or a particular desired set of physical properties in the final product. Theoretical analysis requires a rheological model, which describes reasonably well the flow behavior of the materials under consideration. Hence, given a flow field of a particular material, the development of an acceptable rheological model is very important to the success of theoretical study of flow problems which will be useful for designing better processing equipment and determining optimal processing conditions (Ariff, 2003).

2.2 Polymer Composites Rheology

Einstein, first predicted the effect of filler on the viscosity of a Newtonian fluid. If the liquid phase is a non-Newtonian fluid suspension, its rheological behavior will become even more complex (Garces et al., 2000). Polymer raw materials that are processed into practical product commonly do not consist only one constituent, i.e. 100 percent virgin polymer. They are usually filled with inert particles to enhance the mechanical properties and to reduce cost of final product.

Filler and reinforcement have always played an important role in the modification of polymers to make the polymers suitable for wide variety of end uses and to improve processability (Maiti² et al., 2003). Recently, polymer scientists have become very interested in composites rheology because of the need to develop and process new composites materials with desired physical and mechanical properties. The inclusion of filler, however, makes processing of polymers become more difficult.

The rheological behavior of composites materials not only governs the performance of the end-product but also controls the fluid and heat transfer characteristics during polymer processing. The rheological behavior of filled polymers strongly depends on a large number of parameters such as volume fraction, shape and size of particles, filler-filler and filler-matrix interactions (Boutahar et al., 1996). And recently, filler treatment has become very popular research in modifying the composites rheological behavior.

Filler can be categorized into two parts. First is the non-reinforcing filler which act as a cheapener where it is commonly used in the daily commodity product. While the other is reinforcing filler such as talc and mica for example, introduce higher stiffness while also increasing weight and melt viscosity and decreasing toughness, optical clarity and surface quality. Glass fiber reinforcement provides high stiffness with a corresponding increased difficulty in fabrication and cost.

Typically, the addition of a reinforcing filler to a polymer results in increased modulus but reduced toughness and poorer rheological properties (Garces et al., 2000) Increase in viscosity will result in processing difficulties. Besides filler, the effects of polymer molecular structure or composition on the flow curve can be generalized with the other major factors influencing polymer viscosity as shown in Figure 2.1.

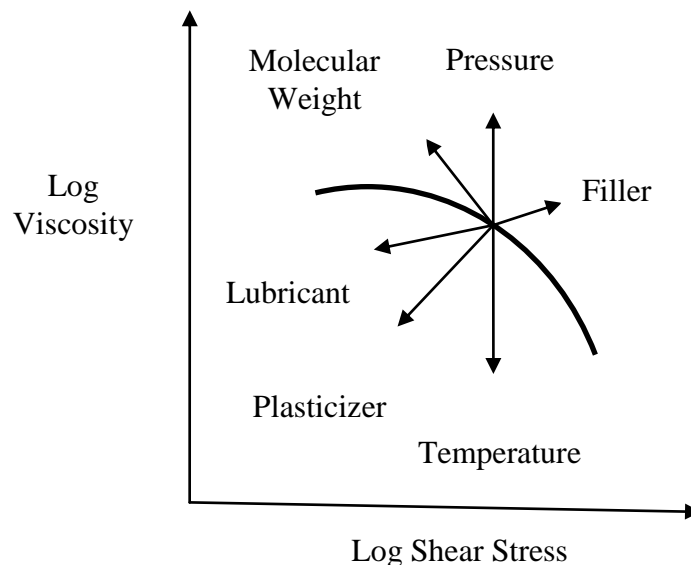


Figure 2.1: Summary of factor affecting the viscosity of polymers (Ariff, 2003)

Various studies have been conducted to understand the rheological behavior of polyolefin composites using mineral fillers such as Suh and White, (2006) who has done extensive investigation of particle orientation influence on rheological properties of talc-filled thermoplastic in both shear flow and uniaxial elongational flow using several equipment such as capillary rheometer, sandwich rheometer, cone-plate rheometer, parallel rheometer and elongational rheometer.

While, Wang and colleague, (2004) studied the effect of processing conditions on rheological properties of polypropylene/clay nanocomposites modified with maleated polypropylene compatibilizer. Since PP macromolecules do not have polar groups, the homogeneous dispersion of hydrophilic particle in PP is difficult. For this reason it is necessary to modify the system so that the filler and matrix have proper interaction and dispersion. Due to this matter, a compatibilizer agent is usually introduced to act as a compatibilizer or wetting agent between the filler and PP.

Among highly use compatibilizer in polyolefin is maleic anhydride-*graft*-polypropylene (PPgMA). Several previous researches done have prove that PPgMA has become an effective compatibilizer even in small amount (Ariffin et al., 2008 and Samsudin et al., 2006). Moreover, there are also researcher claims that the present of MA content (4.2%) does improved the composites mechanical strength. Whereas, most agree that the amount of maleic anhydride composition for individual maleated PP to be incorporated into PP has to be optimize in order to get a desired good processing abilities without sacrificing the overall composites properties and they also claim that the incorporation of PPgMA has lower down the composites viscosity depending on the

amount used (Reichert et al., 2000; Liaw et al., 2008; Denev et al., 2009). Others mainly studied the effect of several parameters such as the filler loading, pressure, temperature and thermoplastic blend ratio (Lee et al., 2003; Leong et al., 2004; Liang and Ness, 1998).

Although many studies have been conducted on polymer composites rheology, the results and discussion may varied from one to the others with respect to arguments on several rheological findings. But, overall conclusions agree that the inclusion of filler will definitely alter the melt flow properties of the main polymer matrix and these giving us the opportunities to modify polymer composites to the desired end product with specific properties. However, parameters of processing have to be controlled sufficiently to avoid processing difficulties which leads to poor product appearance and performance.

2.3 Application of Rheology to Polymer Processing

Generally, polymer processing operation resembles those of classical mechanical or chemical unit operation which simultaneously involve momentum, energy and mass transport of the polymeric materials and some common importance of polymer operations include extrusion process, injection molding, blow molding etc. However, due to special characteristics that the material posses, normally polymer processing operations are far more complicated than other mechanical and chemical engineering unit operations. Therefore, the operation required a large knowledge in several fields of science and engineering that include polymer chemistry, mechanics of non-Newtonian viscoelastic fluids and macromolecular behavior under deformation which is often accompanied by heat and mass transfer and chemical reaction (Garge, 2007).

Figure 2.2 illustrates that there are number of areas have to be covered in order to assist better understanding of rheology in polymer processing operations. One of the areas is to characterize polymeric materials especially their viscoelastic properties by using the existing rheological measuring equipment or developing new rheometers. Better understanding of the rheological properties will gain lots of information in determining molecular weight and also molecular weight distribution of the investigated polymer in providing the optimum processing condition to achieve specific desired set of physical properties in the final product (Brydson, 1970).

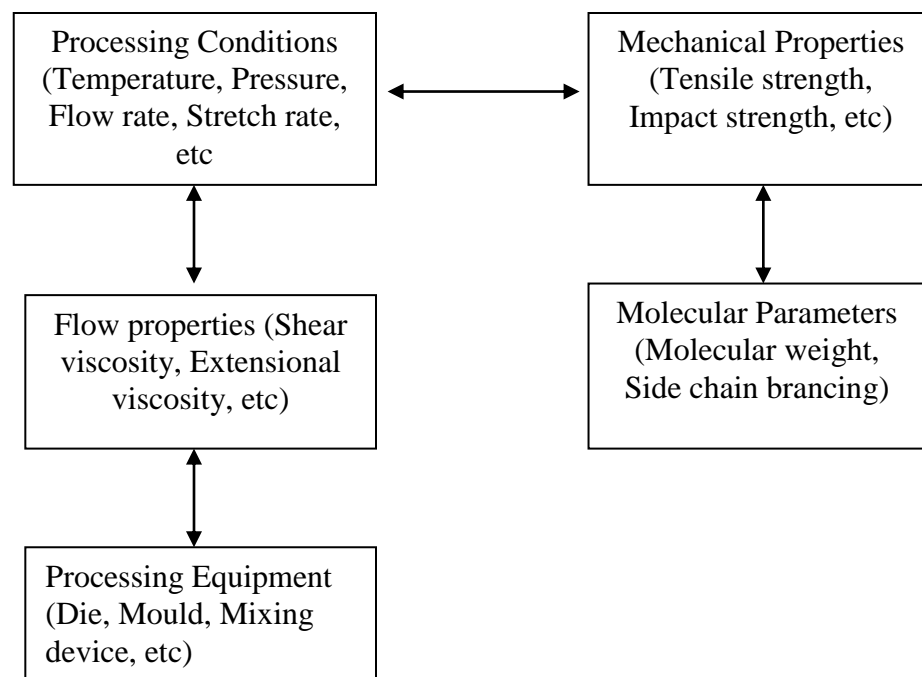


Figure 2.2: Schematic of the interrelationship that exists between the processing variables and flow properties, and between the molecular parameters and flow properties

Besides, by having knowledge of polymer rheology it will probably help in determining the optimal design of processing equipment such as extrusion die, screw of an extruder, various moulds for injection moulding and mixing devices. A proper design of processing equipment requires information of flow properties of the materials under consideration. Furthermore, one needs rheological information to carry out a theoretical analysis of flow mechanics. Theoretical analysis requires a rheological model which describes reasonably well the flow behavior of the material under consideration. Such a theoretical study should be useful for designing better processing equipment and determining optimal processing condition (Ariff, 2003).

2.4 Fundamental of Polymer Rheology

Rheology is a term used to establish relations among the stress state of a body, the strain and the rate of strain. Stress is defined as a force per-unit area and there are two types of stresses. First, is a normal stress that acts in a direction perpendicular to a face and second shear stress that acts in a direction parallel to a face. A clear view of the acted stress is display in Figure 2.3 (Gupta, 2000)

Basically, there are a total of 18 components of stresses due to each stress vectors can be resolved into three components parallel to the three coordinate axes. Nine of the 18 components can be represented using a 3x3 matrix which familiarly known as the stress tensor (σ_{ij}), where i , identified the surface on which the stress acts, while j , identifies the direction in which the stress component acts.

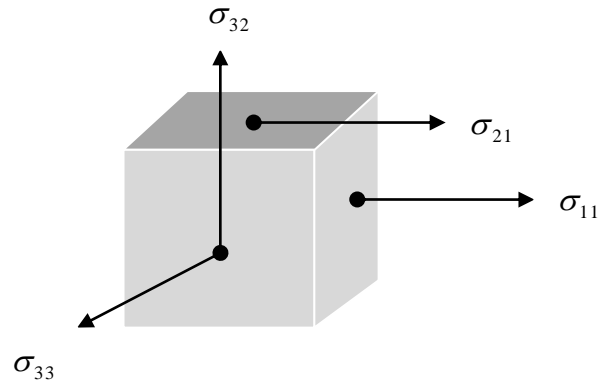


Figure 2.3: Illustration of stress component. (Gupta, 2000)

The other nine components of the stresses are the same as these nine, but they act on the opposite faces.

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \quad (2.1)$$

It is common practice to define the first and second normal stress difference in Equation 2.2 and 2.3.

$$\text{First normal stress difference } N_1 = \sigma_{11} - \sigma_{22} \quad (2.2)$$

$$\text{Second normal stress difference } N_2 = \sigma_{22} - \sigma_{33} \quad (2.3)$$

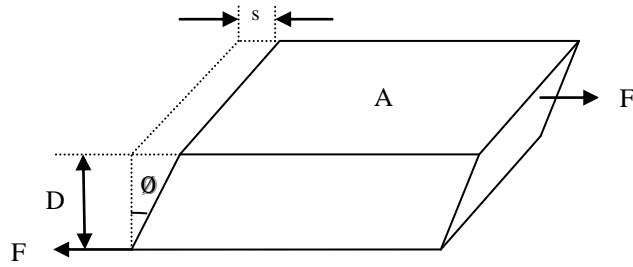


Figure 2.4: Schematic diagram for the measurement of shear viscosity.

All the motion in a viscometric flow is along one coordinate direction, say x_1 and the third direction is neutral. This is shown in Figure 2.4 where a liquid is confined between two plates of area (A) separated by a distance (D). When the upper plate is moved in the x_1 direction relative to the lower plate, the liquid is sheared with the amount of shear rate ($\dot{\gamma}$) being defined as display in Equation 2.4 and 2.5.

$$\dot{\gamma} = \tan \theta = \frac{\text{Amount of sheardisplacement, } S}{\text{Distance between shearing surface, } D} \quad (2.4)$$

The rate of shear strain will then be,

$$\dot{\gamma} = \frac{\text{Relative velocity}}{\text{Distance } D} \quad (2.5)$$

While, the shear rate defined in Equation 2.5 can be generalized to three dimensions by defining the rate-of-strain tensor $\dot{\gamma}$ as shown in Equation 2.6 where the shear rate is simply the 1,2 component of $\dot{\gamma}$. For a Newtonian liquid,

$$\dot{\gamma} = \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (2.6)$$

Therefore, the non-zero component of shear rate tensor is written in Equation 2.7,

$$\dot{\gamma} = \frac{dv}{dx} \quad (2.7)$$

From this set of equations, it is possible to derive the shear rate expression at circular die wall and is given in Equation 2.8.

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \left(\frac{3}{4} + \frac{1}{4} \cdot \frac{d \ln Q}{d \ln \tau_w} \right) \quad (2.8)$$

The detailed derivation of Equation 2.8 involves calculus manipulations and can be found in various rheology textbook (Brydson, 1970; Micheali, 1992). Alternatively, Equation 2.8 can be simplified to the form expressed in Equation 2.9.

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right) \frac{4Q}{\pi R^3} \quad (2.9)$$

where,

$$n = \frac{d \ln \tau_w}{d \ln Q} \quad (2.10)$$

Equation 2.10 suits both Newtonian and non-Newtonian fluids. As discussed previously. For Newtonian fluid, power law index, n, equals to unity and substituting this value will further simplifies Equation 2.11

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \quad (2.11)$$

2.5 Effect of Viscosity Measurement

Since polymer melt are a non-Newtonian fluid material, various effects has to be taken into account to ensure the data measured are reliable and accurate in order to implement it on the actual processing conditions. Normally capillary rheometer is used to obtain the polymer rheological data especially in shear viscosity. In another way, extruders are also capable in providing the apparent flow curve with conditions of sufficient data is provided. Despite its limitation in data generation, extruder may provide data directly base on the actual processing condition and since polymer is a complex fluid, there are various

factors contribute during the data measurement and there are discussed as follow (Gang Yang, 1991).

2.5.1 Elastic Effect

It is well known that polymer is a viscoelastic material. In polymer melt processing, both viscous and elastic component will be deformed and this would bring about the occurrence of phenomena that are associated with elastic response of the polymeric material. During flow of polymer melt, the melt will travelled from a large reservoir (i.e. barrel) to very small die geometry under the application of shear forces. Since polymer melt is a high molecular weight fluid existing in a form of long chain, the molecules can only slide among each other under sheared.

Under normal circumstances, entanglement between molecules prevents the molecules from sliding past each other. When shear forces are introduced, the chains will uncoil and the melt will start to move. On release of the applied shear stress, the chains will recoil and in addition, they can be pulled back by restraining forces i.e. the molecular orientations. Therefore these explain of the most common effect regarding the melt fracture and swelling behavior of the polymer (Ariffin et al., 2006).

2.5.1.1 Extrudate Swell

The most common defect occurring during polymer processing such found during extrusion process is the diameter of the extruded product appears to be larger than the

capillary diameter. As discussed earlier, extrudate swell is strongly related to elastic recovery of the material at the inlet of the die or formerly known as Barus effect. Newtonian liquids can also display a die swell, but only at high rates of flow and as the flow rate decreases the swelling decreases.

For non-Newtonian liquid or elastic liquid, the swelling ratio increases with increasing flow rate. This swelling behavior is highly affected by a number of factors such as temperature, load, length to diameter (L/D) of the die, etc. There are some useful conclusions made by studying by the die swell behavior of common polymer melt (Ariffin et al., 2006; Samsudin et al., 2006)

1. Die swell increase with a shear up to a limit which is near a critical shear rate. Beyond this, die swell decrease as illustrates in Figure 2.5.

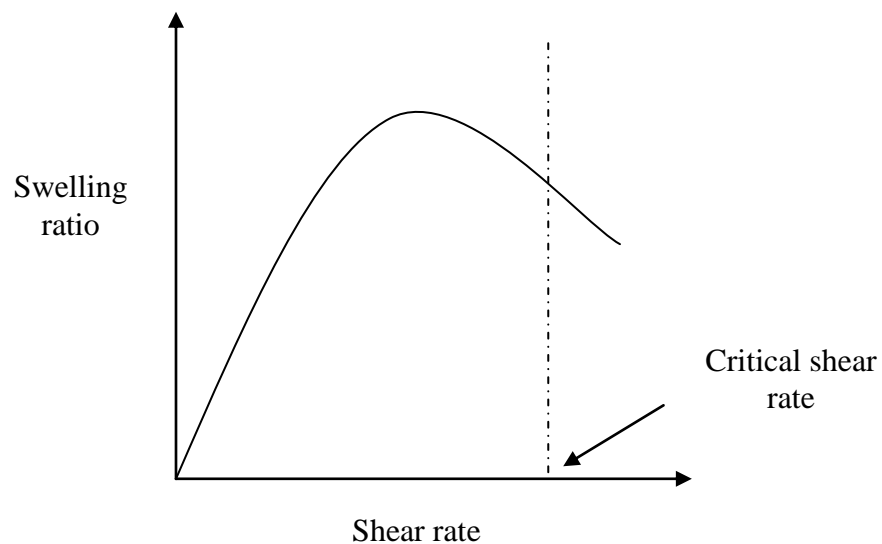


Figure 2.5: Typical form of die swell vs. Shear rate (Garge, 2007)

2. At fixed shear rate, die swell decrease with temperature but the maximum swelling ratio increases with temperature.
3. At fixed shear stress, die swell is slightly affected by temperature.
4. At fixed shear rate, die swell decrease with the length of the die as shown in Figure 2.6

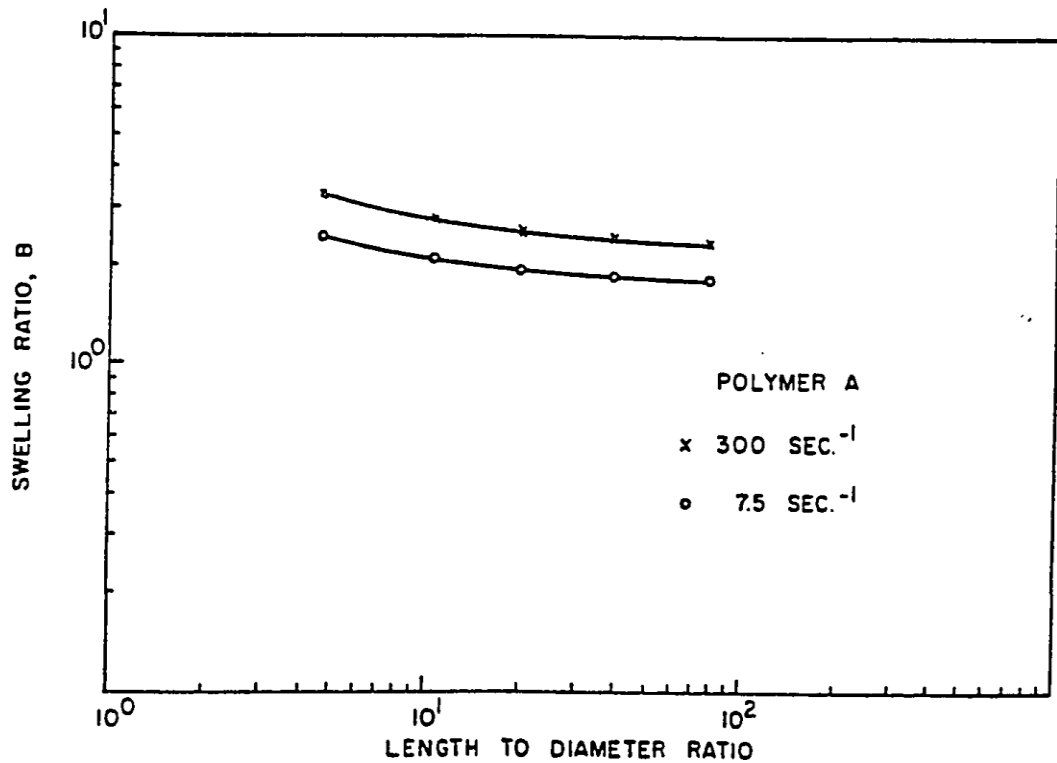


Figure 2.6: Swell ratio against capillary L/R for HDPE (190°C) (Gang Yang, 1991)

5. The greater the resident time in the barrel or capillary die, the less the die swell will be for the extrudate.
6. The greater the shear strain occurs in the capillary die, the less the die swell