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Rheological Behaviour of Polypropylene Through Extrusion and Capillary Rheometry

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1. Introduction

For the past decade, polypropylene (PP) has become one of the most widely use polyolefin especially for intensive activities in research, product development and commercialization. The factor is strongly contributed by the high demands and usage predominantly in food packaging, automotive industries, fabrication of electric and electronic components and currently its utilization in building structural component for civil needs. Despite their variety in terms of its applications, PP has to be brought into melted stage first before it can be transformed into desired shapes. PP possesses relatively high melting point, low density, high tensile modulus and it is relatively low-priced compared to other thermoplastics. In addition, commercial PP consists of generally linear molecular structure thus it can provide low melt strength and exhibits no strain hardening behaviour in the melted stage. This suggests that PP is suitable for injection moulding, blow moulding and extrusion processing techniques (Rahim^a et al., 2011).

During the melt processing, polymeric materials are subjected to various rigorous conditions such as high shear deformation and relatively high temperature that could trigger chemical transformation which subsequently leads to molecular degradation and structural development as well as flows through narrow and complex geometries (Ariff, 2003). These factors will definitely influence the rheological behaviour or to be specific the melt viscosity of PP. If the viscosity of molten PP is not suitable within the processing conditions, short shot or flashing may occur in injection moulding. These problems are essentially crucial to be addressed since the modification on thermoplastic viscosity will also modify the end properties of the produced product. Upon the conversion, there are discrete or usually combinations of chemical and physical changes taking place such as chemical reaction, flow or a permanent change which will directly affect the product end properties. With regards to its flow behaviour, a better understanding of PP rheological characteristic can overcome the existing difficulties and literally secure a successful processing.

Moreover, because of the special characteristic (i.e. viscoelastic behaviour) that PP owns, the processing operations are usually more complex than mechanical of chemical engineering

unit operations. In PP melt, both viscous and elastic component will deform and this would bring about scenarios that are associated with elastic respond of the polymeric materials which are commonly known as melt fracture or flow instabilities. These phenomena can be easily demonstrated by extruding PP melts through capillary or extrusion die above and below the critical wall shear stress. Another common elastic effect occurring in polymer processing besides flow instability is extrudate swell. It is the most common defect found during extrusion process where the diameter of the extrudate appears to be larger than that of the die (Ariffin et al., 2006). Nevertheless, the knowledge of PP rheological behaviour will equip manufacturers with better quantitative processing responses to cater the actual processing complexity.

2. The importance of polymer rheology

Before PP is turned into product, it will undergo fabrication processes that involve deformation and flow which can be said to be the essence of rheology. Polymer rheological data is used in determining whether or not a type of polymer can be extruded, moulded or shaped into a practical and useable product. Having knowledge of polymer rheology would probably help in determining the optimal design of processing equipment such as extrusion die design, screw geometries of an extruder, various mould cavities for injection moulding and mixing devices. This indicates that in polymer processing operations, an understanding of polymer rheology is the key to efficient design, material and process selection, efficient fabrication and satisfactory service performance. Fig 1 further shows numbers of area where a better understanding of polymer rheology can lead to successful polymer processing operation. (Han, 1976)

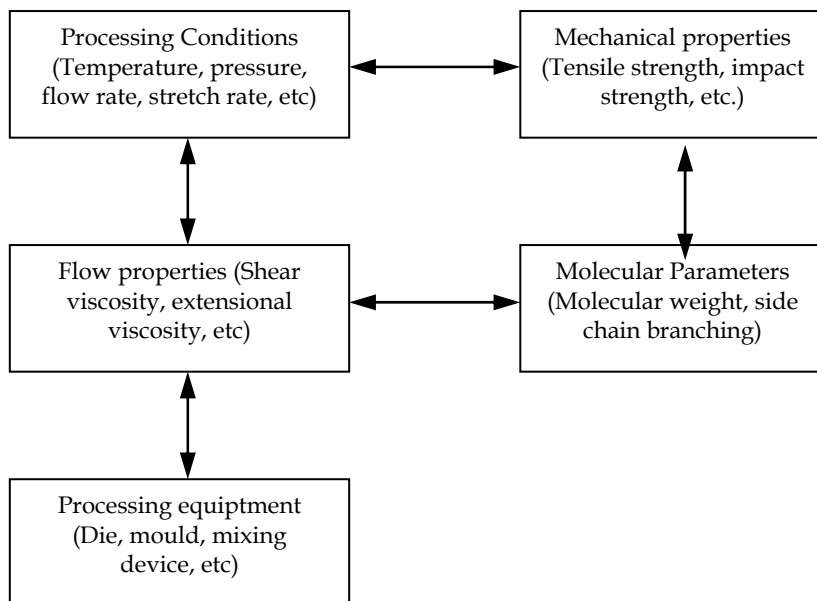


Fig. 1. Schematic of the interrelationship that exists between the processing variables and flow properties, and between the molecular parameters and flow properties (Han, 1976)

Currently there are numbers of methods and instruments available to measure the rheological data of polymers. Since PP is a pseudoplastic thermoplastic fluid that requires relatively high processing temperatures to achieve suitable melt viscosity, it demands a rheological measurement instrument that is able to operate at such temperature under wide of shear rate range. In view of this, capillary rheometer is the simplest and most popular rheological instrument used to measure PP rheological properties (Rahim, 2011; Ariffin et al., 2008; Liang and Ness, 1998; Muksing et al., 2008). This is due to the fact that it has number of advantages over other types of rheometers. First, it is relatively easy to fill which is crucial when dealing with high viscous melt at high processing temperature. Second, the shear rate and flow geometry are similar to the actual condition found in processes such as extrusion and injection moulding (Gupta, 2000). Basically, there are two types of capillary rheometers to measure the viscosity of molten PP namely the pressure-driven type (constant shear stress) and the piston driven type (constant shear rate), yet the approach of their measurement procedure is quite similar where it depends on the applied force (Fig. 2).

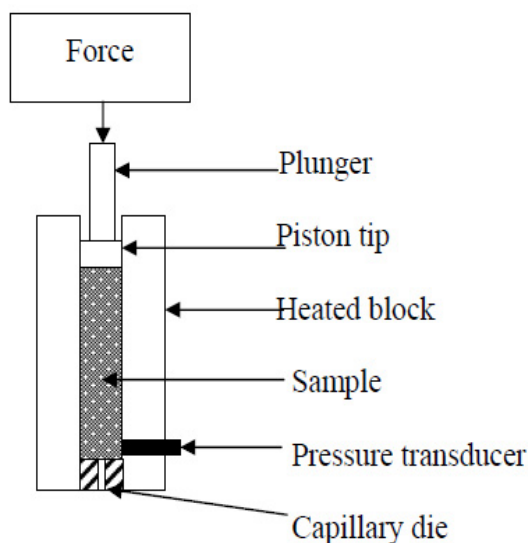


Fig. 2. Schematic diagram for capillary rheometer

The deformation and flow from shear mechanism introduced during polymer processing will results in molecular orientation which creates a dramatic effect on the physical and the mechanical properties of the moulded parts, profile extrudates, film, etc. The kind and degree of molecular orientation are largely determined by rheological behaviour of the polymer and the nature of flow in the fabrication process. Furthermore, PP is a semicrystalline material which always be affected by the application of shear stress under the action of shear flow during processing. Simultaneously upon solidification, the generated shear flow will bring a profound effect on the nucleation and crystallization of polypropylene. Crystallization process involves the transportation of molecules from disordered liquid to ordered solid stage. It is a unique phenomenon which occurs due to chain orientation of PP molecular structure. In recent years, many experimental results have

confirmed that the orientations of the polypropylene molecules are strongly affected by the flow field acting on the molten PP (Jikan^a et al., 2010; Jikan, 2010; Rahim^b et al., 2011).

Other than experimental or practical assistance, rheology can also be a great help to polymer processing in carrying out theoretical analysis of the mechanics of flow of rheologically complex of polymer in various kind of processing equipments. Theoretical model requires rheological models which describe reasonably well the flow behaviour of polymeric materials under consideration. Hence given a flow field of specifically PP, the development of an acceptable rheological model is very important to the success of theoretical study of flow problems. Such a theoretical study should be useful for designing better processing equipment and determining optimal processing conditions. Reviewing the mentioned importance, one should note that behind the complexity of rheology measurement there is significant importance that makes rheological studies unavoidable to polymer scientists and polymer design engineers (Ariff, 2003).

3. Factors affecting the rheological behaviour of polypropylene

Previously, many have reported (Gonzalez et al., 1998; Liang, 2008; Brydson, 1970) on factors affecting the rheological behaviour of PP. Basically, reports usually regulate around four fields of studies. The first field of study involves molecular structure influence on rheological behaviour of PP such as the type of backbone chain, chain branching and chain branching configuration. The second area which is the most likely favoured by researchers is the study on how composition of polymer system or heterogeneity affects rheological behaviour such as those found when PP are blended with other polymers, addition of fillers and other additives are also of interest. The third part involves the study on the dependence of PP rheological behaviour towards fabrication process parameters like pressure, temperature and equipment's geometrical factor. Lastly, the fourth covers the PP theoretical analyses using various rheological models of PP and their implementation in simulation software which regulates around all three fields of studies previously discussed. The extent of these factors will be forwarded in the following sections.

3.1 Molecular structure of polypropylene

PP can be made from the propylene monomer by a process known as Ziegler-Natta catalyzed polymerization or by metallocene catalysis polymerization. PP is a linear hydrocarbon polymer that contains little or no unsaturation in its chain structure. Structurally, it is a vinyl polymer with every other carbon (C) atom in the backbone chain is attached to a methyl (CH₃) group. Compared to polyethylene, PP has some similarities in their characteristics such as swell in solution. The characteristics of PP vary according to the molecular weight and grade. The Ziegler-Natta catalysts have several active sites and accordingly the obtained PP exhibits broad tacticity and molecular weight distributions. It is discovered that by using different types of catalysts and polymerization methods, the molecular configuration can be arranged to produce three types of PP (Jikan, 2010; Karger-Kocsis, 1995).

Mechanical properties, solubility and melt level can be ascertained with knowledge on polymer tacticity. (Andres et al., 2007). The presence of methyl group in PP backbone chain can provide various differing characteristics for PP, depending on the arrangement of methyl group in PP carbon atom, whether in isotactic, syndiotactic or atactic configuration

(as shown in Fig. 3). This tacticity will dictate the viscosity of PP that directly contributes to different end properties. Most (90-95%) of commercial PP are isotactic PP produced by Ziegler-Natta catalyst with head-to-tail incorporation of propylene monomer. Isotactic configuration is the most stable structure since the methyl group is arranged at only one side in the PP chain structure. This structure prevents PP from crystallizing in a zig-zag planar shape, but rather in helical crystal structure. With those conditions, the degree of crystallization of isotactic PP can normally reach up to 50% that causes an increase in PP softening temperature which means an increase in the melt viscosity throughout the processing procedure. However, the presence of methyl group attach on the PP backbone are easily oxidized when high processing temperature is utilized and these sites are prone to be chemically attacked by certain chemical agents.

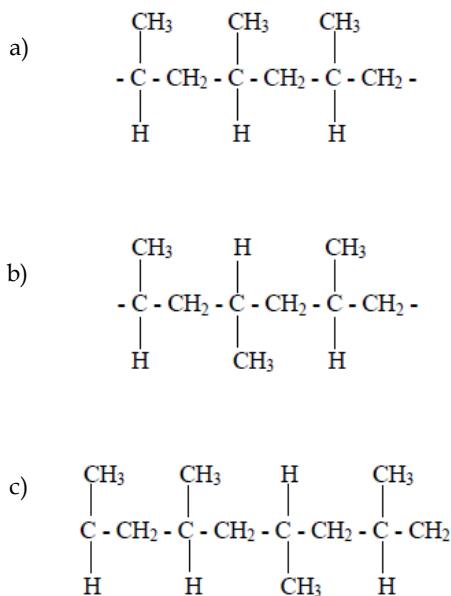


Fig. 3. The three basic structures for polypropylene (a) isotactic, (b) syndiotactic and (c) atactic.

However, PP chain configuration is directly related to density which can be classified in many forms such as homopolymer, copolymer with ethylene, or homo- or copolymer blended (which will be discussed later) with ethylene propylene diene monomer (EPDM) rubber or known as thermoplastic polyolefins (TPE-O or TPO, when elastomeric properties appear at higher levels of EPDM). All these components that exist in either PP side chain or partially associate within the PP matrix will definitely influence the molecular weight (MW) and molecular weight distributions (MWD) of the produced PP. It has been revealed in Fig. 4 that the viscosity of PP copolymer (with ethylene monomer) is much lower than that of homopolymer PP obtained using twin screw extruder. The developed viscosity curve has shown to be strongly dependent on the molecular architecture of PP backbone which is well associated with polyethylene group link to its backbone. Higher amount of side group i.e. the methyl side group has fairly raised the disentanglement to the PP polymer chain and caused

reduction to the chain mobility. This indicates that the viscosity of PP is virtually dependent on the irrespective molecular chain characteristic (Gonzalez et al., 1996; Andres et al., 2007).

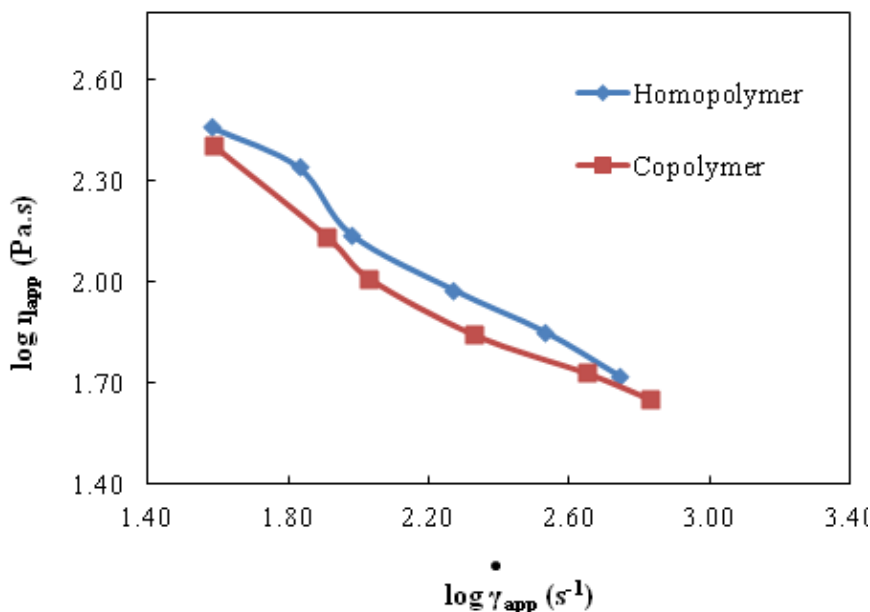


Fig. 4. Viscosity flow curves of PP copolymer (with ethylene monomer) and PP homopolymer obtained using a twin screw extruder

Moreover, the types of manufactured PP differ resulted from their large range of MW. Higher MW usually indicates the existence of longer molecular chains that provide more points of contact or even entanglement between chains. Short branches normally do not affect the viscosity on the molten PP significantly compared to long branching system. Such branching reduces the viscosity of the polymers yet unlike LDPE, PP branch is greater that they can take part in formation of entanglement (Bydson, 1970; Samsudin et al., 2006; Ariff, 2003). Depending on the degree of chain entanglement, it is more likely that a secondary crosslink or known as physical crosslink would form and cause reduction in the mobility of PP molecules. Due to that matter, high shear forces are required to move these PP melts. Gotsis and co-workers has systematically approved that branches existing in polypropylene has increased the zero shear viscosity and increase the polypropylene melt elasticity and improve the melt strength (Gotsis et al., 2004). Hingmann and Marczinki have suggested that the PP shear viscosity increased with chain branching using the Lodge Model (Hingmann and Marczinki, 1994). Meanwhile, Ogawa has finalised that the higher the PP molecular weight, the higher the PP mechanical properties will be (Ogawa, 1994).

In recent years, many researchers (Azizi et al., 2008; Samsudin et al., 2006) are aware and have made considerable interests in dedicating their work in modifying the chain configuration of PP to alter the melt flowability of the material. The most preferred method is by additions of degradation substance such as peroxides. These peroxides are introduced to control the rheological behaviour of PP by lowering the viscosity of the viscous PP melts

during processing. Previously, Azizi and colleague has soundly concluded that the addition of high amount dicumyl peroxide has significantly reduced the melt viscosities of PP using either MFI or twin screw extruder. They also found that the addition of peroxide has subsequently lowered the MW and MWD of PP by chain scission reactions which has shortened the PP chain length consequently leads to decreasing values of PP viscosities. The statement is in good agreement with Berzin et al. who also claimed that PP molecular weight distribution are narrowed and high molecular weight species has decreased when the amount of peroxide was increased which enable it to form free radical during thermal decomposition (Berzin et al., 2001).

Another common way to configure the chain achitecture of PP is by thermal, mechanical, oxidative or combinations of these mechanisms. Initially, the identification of these mechanisms would equip manufacturers with good information in selecting PP processing conditions either to promote or to prevent it. It was demonstrated by Gonzalez et. al that during multiple extrusion of PP, MW and viscosity can be reduced with increasing number of extrusion cycles. The chain scission is thought to be provoked by thermomechanical reactions rather than degradations (Gonzalez et al., 1998). On the contrary, PP which contains tertiary hydrogen atoms are most susceptible to oxidation reactions. Other than chain scission, PP also has the tendency to form a crosslinking. The reaction is highly contributed by radical-radical combinations where it literally increase the MW and MWD. Traditionally, intrinsic viscosity measurement were implemented as an indicator of the MW of a PP. However, intrinsic viscosity test have been largely replaced by gel permeation chromatography (GPC) which enables a direct assesment of MW. The occurence of PP crosslinking are commonly found during multiple extrusions with the contributions by various enviromental factors and radiation (Scheirs, 2000).

3.2 Composition or heterogeneity effect of polypropylene

The composition or heterogeneity effects are classified as external factors since all of them are included during the mixing process. One of the factors involving the composition of polymer system includes addition of one or more system which known as blends. Consequently, PP blends have been extensively studied and developed by many researches for the past 20 years either with thermoplastic or elastomeric materials such as ethylene-propylene copolymer (EPR) and ethylene propylene diene monomer (EPDM). Blending is a common useful method to improve PP properties but it is not as simple as adding other polymers into an extruder and mechanically mixing them in the molten state. Typically, morphology and compatibility issue as well as processing difficulties which closely related to flow ability of the blends will rise. The viscosity may increase and decrease depending on the structure of the added block of polymer into the molten PP. Normally the increase in viscosities are caused by the addition of immiscible block like styrene or by the change of bulk properties or the addition of blend component that enhanced the degradation effect in PP blends (Keawwattana, 2002).

The second types of blends that can be produced are miscible blends where the blend may have a higher viscosity than PP and appears to be remarkably elastic. The chemical structure of the miscible block appears to be more important in governing the observed viscosity of the system where it has increased the viscosity of the system. For instance, Song et. al has shown that the rheological behaviour of blend PP and POE (polyethylene-1-octene) is highly

depended on the blend ratio of the system. Higher dynamic complex viscosity and loss modulus were observed for the blends with portions of 10 wt% and 20 wt% PEO where miscibility was achieved. Later on, incorporations of higher content of PEO have subsequently reduced the dynamic complex viscosity and loss modulus which attributed to the immiscibility between the two matrices (Song et al., 2008). Besides miscibility, the increase in viscosity of PP blends can also correspond to the effect of crosslinking of the other blend materials. Previously, the rheological behaviour of PP-natural rubber blends was investigated by Thitithammawong and co-workers. They have found that the shear stress and the viscosities of the blends have increased as a result of crosslinking of rubber molecules (Thitithammawong et al., 2007).

On the other hand, filler and reinforcement have always played an important role in modifying PP properties. Fillers incorporated inside PP matrix is purposely to reduce overall cost, improving and controlling process characteristic, density control, dimensional stability and etc. The inclusion of fillers into PP can affect almost all of its properties which also include surface, colour, expansion coefficient, conductivity, permeability, mechanical and rheological properties. Many factors influence the behaviour of fillers in PP melts. The type, compounding method and loading of filler dictate its effectiveness. Fillers can be categorized into two groups, i.e. inert fillers which act as cheapeners and reinforcing fillers that are sometimes used in engineering applications. Among these types of fillers are mineral fillers such as calcium carbonate, talc and kaolin which are most commonly used in PP (Ariffin et al., 2008). The addition of these fillers in PP however, would bring a significant change in the rheological properties such as the viscosity of the base resin. From Fig. 5, it can be seen that the viscosities of PP-kaolin composites have risen as the addition of higher kaolin content measured using a Melt Flow Indexer (MFI) at 210°C. This fact is attributed to the substitution of PP matrix which consists of flexible molecules with more rigid kaolin particles. The ease of melt flow is highly dependent upon the mobility of the molecular chains and force or entanglement holding the molecules together. As the kaolin loading increases, the PP chain mobility are significantly affected by the overloading of kaolin particles in the system which perturb the normal flow and hinder the mobility of chain segments in melt flow, consequently increasing the value of the apparent viscosity (Rahim^a et al., 2011; Jikan et al., 2009, Rahim, 2010)

Particle shape is another crucial factor in the incorporation of filler in polymer since this affects the polymer characteristics and processing method. Shapes of particles can be categorized as cubic, needle-like (acicular), block, plate or fibre. Spherical particles that flow and disperse well throughout the molten polymer cause the least problem related to stress concentration (Jikan, 2010; Pukanszky, 1995). Needle-like (acicular), fibrous and platy shape fillers can be more difficult to disperse and they can act as stress concentrators, which reduces impact strength (Rothon, 2002). Depending on the filler shape, the addition of fillers at low concentration is able to increase the flow resistance and reduce the built up pressure within the processing equipment. Maiti et al, has mentioned that the apparent viscosity of iPP/CaSiO₃ system exhibited lower shear stress compared to pure PP. The reason was claimed to be interrelated with CaSiO₃ flake-shape. Same scenario was discovered for PP-kaolin composites where kaolin has similar flaky geometry. The flake-like shape of these filler particles make them able to slide within the PP system during the application of shear forces causing a flow-favouring orientation which subsequently lowered the viscosity of PP matrix (Rahim^a et al., 2011; Maiti et al., 2002)

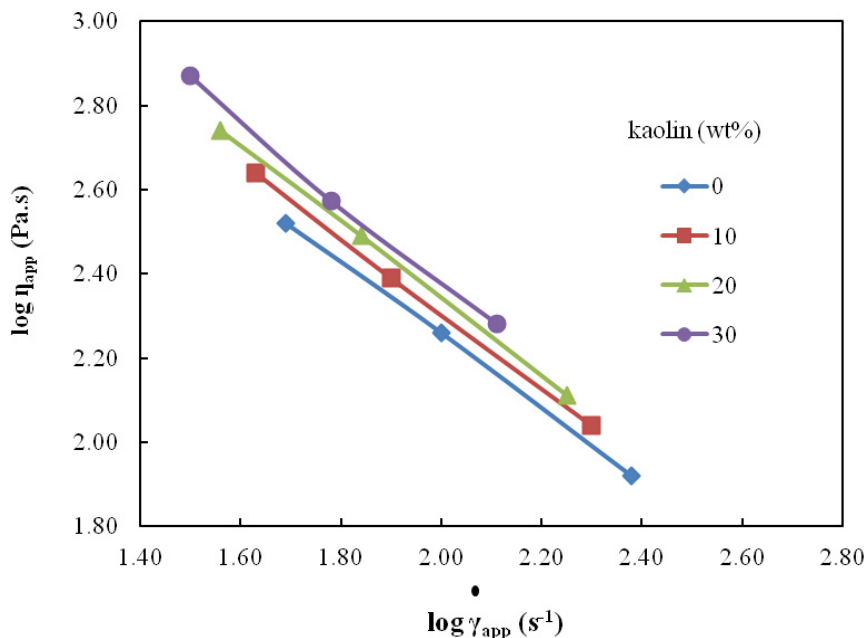


Fig. 5. Viscosity curve of PP-kaolin composites using a Melt Flow Indexer (MFI) at 210°C

Since PP macromolecules do not have polar groups, the homogeneous dispersion of hydrophilic particles in PP is difficult. Therefore, it is necessary to modify the system so that the filler and PP have proper interaction and distribution. To encounter the issue, compatibilizer or coupling agent is usually added to act as a wetting agent between the filler and PP. Among the highly used compatibilizer in PP is maleic anhydride-graft-polypropylene (PPgMA). In the investigation of Liaw et al. the incorporation of PPgMA has reduced the composites viscosity depending on the amount used for PP/clay nanocomposites. To reconfirm the statement, we made an attempt to analyze it with a wide range of shear rate using a capillary rheometer for 20 wt % kaolin loading with the addition of 5 wt% PPgMA and without the addition of PPgMA at 210°C. The claim and our finding is in good approximation where PPgMA has played a role as a flow promoter in PP matrix. The softening effect brought by the maleic anhydride group (MA) content has lowered the system melting temperature. Hence, the decreasing value of the composites viscosities throughout the shear rate range is attributed by the plasticizing effect by the PPgMA in the composites (Liaw et al., 2008).

Other composition factor that affects the processing of PP melt is the inclusion of necessary additives such as plasticizer, lubricant or flow enhancer, environmental stabilising agents and pigment or colorant. The last two usually do not bring significant effect on the flow behaviour of PP melt since they are added in small quantities unless they are able to carry multiple functions which includes plasticizing (similar to PPgMA) and lubricating the compounding system. Nevertheless, the first two additives, i.e. plasticizer and lubricant proved to have a bound effect on the PP melt flow. Due to their ability to dissolve in PP

matrix, they are able to space out the PP molecules thus increasing their mobility and consequently reduce the viscosity of the system. Apart from reducing the viscosity, they also tend to reduce the glass transition (T_g) temperature of PP and elastic modulus of the melt (Liaw et al., 2008; Ariffin et al., 2008; Maiti et al., 2002).

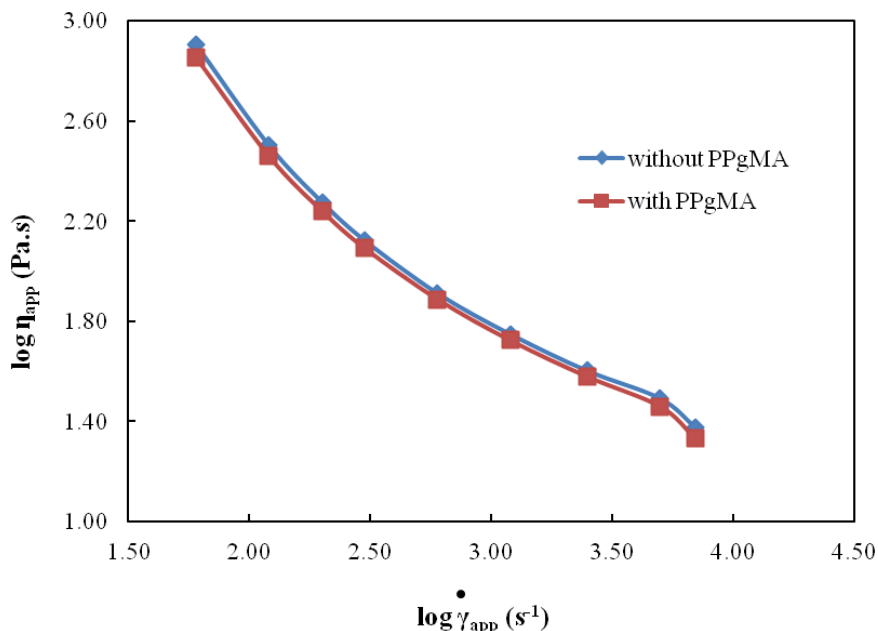


Fig. 6. Viscosity curves of 20 wt % kaolin loading with and without PPgMA for PP-kaolin composites obtained using capillary rheometer at 210°C

3.3 Fabrication process parameters of polypropylene

For the ease of flow, polymer molecules must have enough thermal energy to make it mobile which also associates with having enough space surrounding the molecule which allows it to past other molecules. Thereby, the melting of PP is strongly dependent upon the mobility of its polymer chains. Below T_g , the latter condition is not met, and PP is still in solid state. Above T_g , the magnitude of shear viscosity is totally dependent on the availability of free volume. Whereas at temperature far above the glass transition temperature or the melting point of PP, there is ample free volume available and the temperature dependence of the zero-shear viscosity is determined by energy barriers to motion. A number of researches have come into agreement that the viscosity of PP follows the Arrhenius equation to a good approximation where it is common to observe a decreasing function of viscosity and shear rate that varies considerably (Gupta, 2000).

For isotactic PP, it is expected that the overall viscosity for the high processing temperature is respectively lower than that of at low processing temperature (Fig. 7). From the molecular level, the flow occurs when PP molecules slide past each other. Whereby, the ease of melt flow depends upon the mobility of PP molecular chains and forces of entanglements

holding the molecules together. As the free volume increases with temperature, PP molecules occupy more space due to an increase in the distance between them making it easier to slide among each other and together with the introduction of high shear rate will eventually reduce the PP matrix viscosity significantly (Scheirs, 2000). Similar trend was observed for PP composites system by Rahim^b et al. and blend system of LDPE/PP blends by Liang and Ness where the viscosities of the compounds are lowered at high processing temperature (Rahim^b et al., 2011; Liang and Ness, 1998).

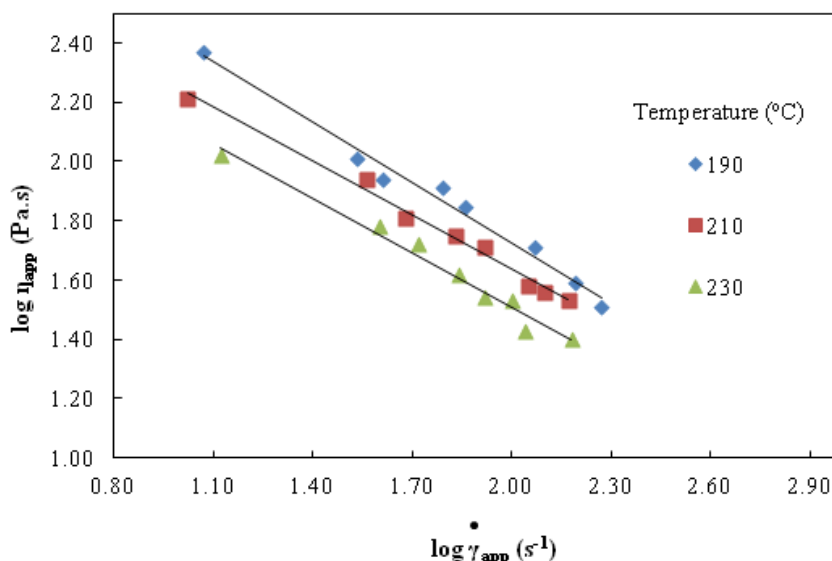


Fig. 7. Viscosity curves of isotactic PP obtained using single screw extruder at various processing temperatures.

In contrast to the effects of temperature and pressure play significant roles in altering the viscosity of polypropylene melt. During polymer processing operations such as extrusion and injection moulding, the applied pressure can reach up to thousands of atmospheres. Large hydrostatic pressure will result in a decrease in the free volume in the melt and accordingly, it should display an increase in viscosity near to polymer T_g . In addition, the reduction of free volume will result in the mobility of polypropylene molecules in the melt to become more restricted. Since viscosity is very dependent towards the distance between each molecule, it is expected that an increasing pressure would increase the viscosity by the way of that a low molecular weight liquids decreases its distance between particle and molecules. Thus, the influence of pressure can be considered quantitatively equivalent to that of temperature but acts the opposite way (Brydson, 1970).

Besides temperature and pressure, in various polymer operations, molten polymer is forced to flow into a wide variety of geometrical configurations; indeed the rheological properties of the polypropylene melt are influenced by the flow geometry (Micheali, 1992; Liang, 2001). Extrusion process have the most critical dependence on flow geometry, where the final product properties as well as appearance is directly related to the geometry or die through

where the molten PP is extruded out which will be further discussed in detail in the extrudate swell sections. Experimentally, a non-overlapping rheological experimental data of viscosity curve of different length to diameter (L/D) die ratios can be observed. The results are more obvious for low ratio of L/D . Theoretically, it should form a single curve despite of the different die geometries since the measurements are implemented on the same material. The cause of this problem is highly due to the existence of large error in pressure drop measurement within the measuring instrument. To address the erroneous pressure measurement, Bagley correction procedure was applied and has proven to be successful not just for PP but also for other thermoplastic materials (Rahim, 2010).

4. Viscoelasticity of polypropylene

Viscoelastic properties, as their name implies, display responses towards an applied stress which is a combination of elastic and viscous deformations. The two most commonly used models are those attributed to Maxwell and Kelvin. Kelvin model describes very well the concept of 'creep' (the change in strain at constant stress), whilst the Maxwell model quite reasonably describes 'stress relaxation' (the change in stress at constant strain). In combination, the elements of Maxwell-Kelvin model display both elastic and viscous (namely viscoelastic) characters at deformation rates in between the two extremes (i.e. low and high rates) in varying proportions. A number of different effects may be noted depending upon the degree of elastic character possessed by a viscoelastic polymer melt (Prentice, 1997). Generally, the relative proportions of each property are highly dependent on the rate of deformation.

It is well known that PP possesses viscoelastic behaviour during polymer processing. Both viscous and elastic component will deform and this would bring about the occurrences of phenomena that are associated with elastic response for PP. During the flowing process, the melt will travel from a large reservoir (i.e. barrel) to very small die geometry under the application of shear forces. Under normal circumstances, entanglement between molecules prevents the molecules from sliding past each other. When shear forces are introduced, the chain will uncoil and the melt will start to move. On release of the applied shear stress, the chain will recoil and in conjunction they can be pulled back by the restraining forces (i.e. molecular orientation). This theoretically explains the most common effect observed during extrusion process involving extrudate swell and flow instabilities which are going to be deliberated in the next couple of sections.

4.1 Extrudate swell

Extrudate swell is strongly related to elastic recovery of PP at the inlet of a die. Newtonian liquids can also display swelling occurrence, but can only be observed at a very high flow rates. Whereas for PP (which is a non-Newtonian liquid), the swelling will increase with increasing flow rate. When a polymer melt is deformed, either by stretching, shearing or often by a combination of both, the molecules chain are stretched and untangled. In time, the molecules will try to recover their initial shape, by then getting used to their new state of deformation. If the deformation is maintained for a short period of time, the molecules may return to their initial configuration and the shape of the melt is fully restored to its initial shape. It can be said that the molecules remembered their initial configuration. However, if

the shearing or stretching goes on for an extended period of time, the molecules cannot recover to their initial arrangement, in essence forgetting their initial positions (Osswald, 1998). Thus, when elastic liquid (such as in PP melt) is extruded from a die or flowed from the exit of a tube, it usually swells to a much greater diameter than that of the die hole. Besides shear rate, the swelling behaviour is highly affected by a number of factors such as temperatures, L/D of the die, shape of the die, filler loading and etc. (Ariffin et al., 2008).

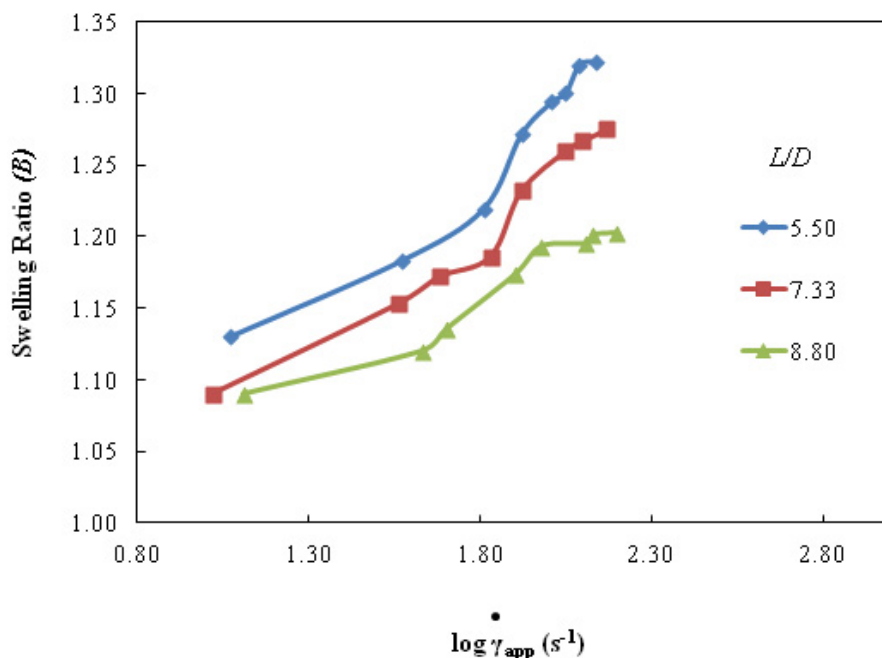


Fig. 8. Swelling ratio of isotactic PP recorded from extrusion process using single screw extruder at various processing temperatures.

One of the affecting parameters for extrudate swell is the influence of die design which is easily illustrated through the die L/D ratio. The extrudate swell phenomenon is indicated by the swelling ratio (B) obtained by dividing of extrudate diameter with the die diameter. For a given rate of flow or shear, the extrudate swell decreases as the L/D ratio of the capillary increases and ultimately attains an equilibrium value as shown in Fig. 8 for pure PP. The root for this condition is the extensional flow at the capillary entrance that imparts greater molecular orientation compared to shear flow within the capillary. Thus, in a long capillary die, some of the molecular orientation imparted to the polymer in the entrance region can relax out in the capillary itself. Also at a constant shear rate, extrudate swell tends to decrease fairly as the temperature is increased since the molecular orientation relaxes faster at higher temperatures (Gupta, 2000). In addition, as the temperature rise, the contributions of viscous component will become more pronounce than that of the elastic component. Furthermore, until it solidifies, the extrudate will sag under the influence of gravity and its diameter will then be reduced. The simplest practice to reduce the extrudate swell is by

using a capillary die with a large L/D ratio that will eliminate the effect of the entrance flow on the swelling extrudate.

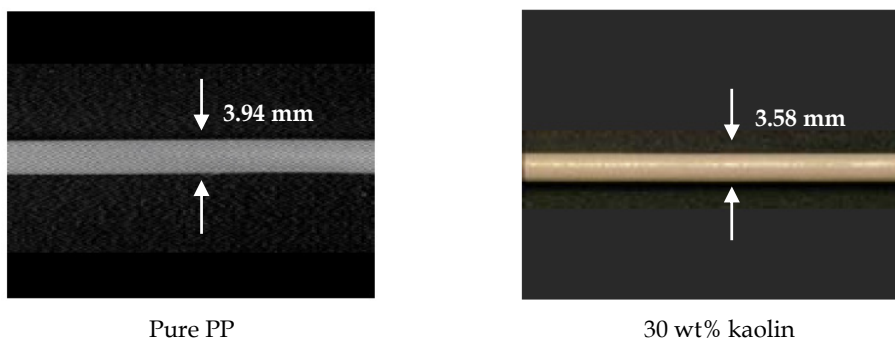


Fig. 9. Swelled extrudates of pure PP and PP-kaolin composites with 30 wt% filler loading for obtained from extrusion process using capillary rheometer at 200°C

It can be observed from Fig. 9 that PP with 30% kaolin loading had predominantly experienced a reduction of extrudate swell ratio. This behaviour can be due to the fact that the PP chain remains unchanged because of the present of filler particles thus providing more oriented and aligned structures. It is obvious that filled compounds offer greater deformation resistance, due to a reduction in mobility of the polymer chains. This concurs with Muksing et al. (2008) who stated in his research that the layer of fillers create molecular chain barrier in vertical plane towards extrusion direction when leaving the capillary die which limits elastic recovery thus causes reduction in extrudate swell (Liang, 2002). Whereas different scenario can be observed in unfilled PP, an increase in deformation rates in this system is generated by greater molecular realignment and reorientation which reduced relaxation of molecules, which leads to enhanced chain rigidity and shattered melt strength. The addition of rigid particulate filler such as kaolin clearly has similar qualitatively effect on the melt strength of thermoplastics, as noted by Tanaka and White (1980).

4.2 Flow Instabilities

Besides extrudate swell, another common elastic effect occurring in polymer processing is flow instabilities such as melt fracture. Distortion of extrudate is a result of polymer molecules reaching their elastic limit of storing energy, thus causing melt fracture as a way of relieving stress either at the die wall or at the die entrance. Another opinion forwarded by White (1973), is that the extrudate distortion is caused by differential flow-induced molecular orientation between the extrudate skin, holding highly oriented molecules, and the core which has no significant molecular orientation. It is of course, possible that the melt fracture occurs due to a combination of the stress relief theory and the differential flow induced molecular orientation (Shenoy, 1999). In conjunction, PP body consists of long chain molecules and when high pressure is applied; the system would simplify the movement of PP molecules to slide past each other. A rapid and random movement of molecules might cause disordered configuration to the chain that allowed deformations to take place. More likely when stress is removed as the extrudate emerge from the die, the elastic behaviour of

the melt flow will struggle to recover predominantly from the elastic memories attained by the large deformation. This elastic property could be seen when extrudate flowing out of the die and it manifest itself in many ways such as the extrudate exhibiting flow instabilities after experiencing extrusion process (Liang and Ness, 1998).

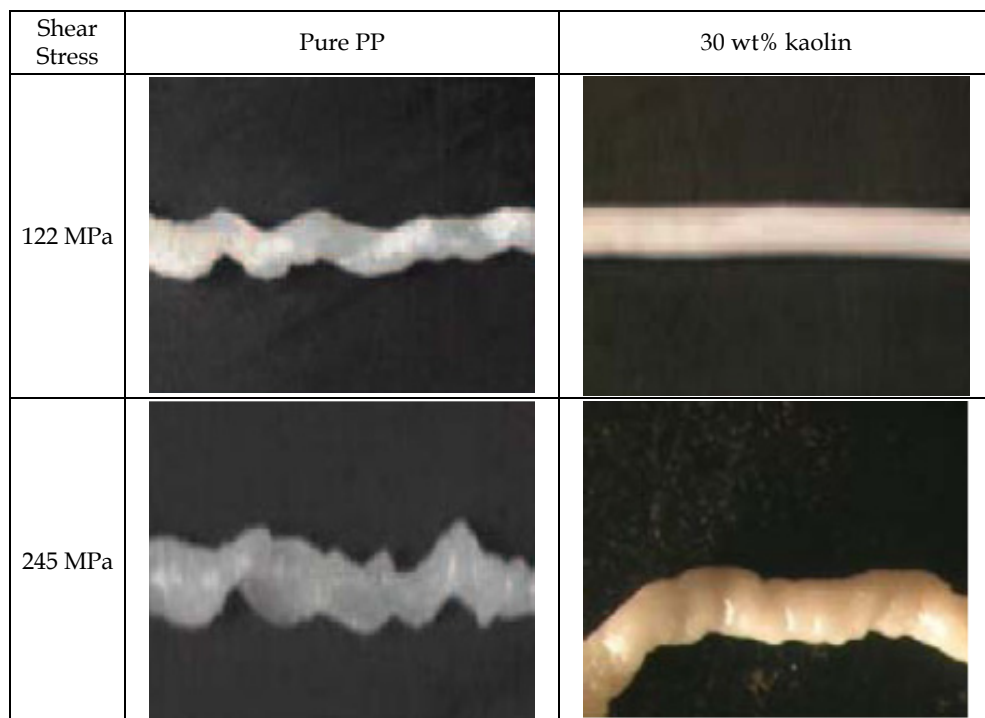


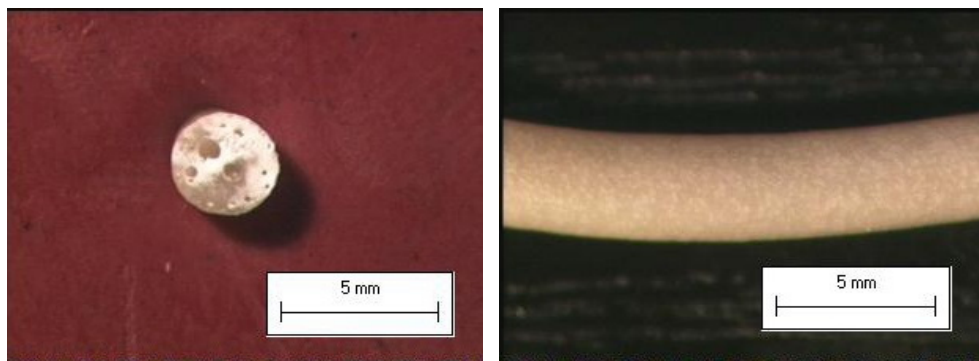
Fig. 10. Flow instabilities of pure PP and PP-kaolin composites with 30 wt% filler loading obtained from extrusion process using capillary rheometer at 165°C for $L/D = 4$

Since the flow instability is more available for shorter die and at lower die temperature, an experiment was conducted using a capillary rheometer at 122 MPa and 245 MPa of shear stress for a capillary die with $L/D = 4$ and at the temperature of 165°C to verify the scene. Based on Fig. 10 for pure PP and 30 wt% kaolin loading for PP-kaolin composites, it has plainly shown that the incorporation of fillers in the composite systems is able to reduce melt flow instability from appearing. This was caused by the presence of a large amount of filler that reduced chain recovery memory by preventing the polymer molecules from returning to their original configuration after stress was withdrawn from the system. Fillers are able to restrict the mobility and deformability of the matrix by introducing mechanical restraint. Whereas, unfilled PP did not have any additional structures that can hold and restrain PP molecules from returning to their original configuration. Furthermore, fillers have the ability to delay melt fracture given that filler particles tend to travel to the surface (skin) of the sample melt thus improving sticking effect between melt and die wall (Gupta, 2000) thus the stick-slip scenario will then be reduced. It clearly elucidates that filler loading highly influences this phenomenon.

Accumulated from the effect of filler loading, preliminary testing has evidenced that low shear stress applied to the sample melt (at low processing temperature of 165°C) was unable to extrude the sample out of the die due to the fact that the system is still in a semisolid state. Nevertheless, different scenario could be seen when the samples were processed using higher shear stress (≥ 122 MPa). It is believed that the ability of extrudate to emerge from die even at semisolid state is brought about by pressure that surpasses the critical shear stress. When exceeding that value, pressure This led to fluctuation in flow propagation which contributed slip or stick phenomenon (Shore et al., 1997). Extrudate with shear stress of 245 MPa shows further distortion compared to extrudate with shear stress of 122 MPa. This means that flow instability increased when shear stress was increased. The flow instability experienced in this research is commonly identified as melt fracture. Normally, melt fracture is caused by nonlaminar or turbulence flow due to the L/D , type of polymer and processing parameter (Cogswell, 1981). During the extrusion process, the flow direction of PP melt in the barrel was in a form of laminar flow. Nevertheless, it started to experience disturbance when entering the die area. This is due to the fact that the melt in the middle of the die entry started to fracture when high shear stress was applied to the system. This led to fluctuation in flow propagation which contributed towards the flow instability experienced by the extrudate surface.

The effect of temperature plays a vital role in reducing the flow instability of PP system. At a temperature well above melting point, molecules start to enhance their movements. The swift activities of these molecules rise the collisions between them and lead to a molecule's repulsion scenario. Simultaneously, these molecules take up more volume given that the space between them has been increased. At this phase, the molecules are in a tranquil state and some of the elastic memory of the system has faded away due to the relaxation condition. Therefore, when shear is applied to the system (at temperature above melting point) molecular chains could effortlessly align themselves according to the flow path without causing any collisions. In this situation, elastic recovery is relatively low or even absent, consequently decreases the deformation rate which is closely related to the flow instability mechanism. On the contrary, most of the extrudate surfaces exhibit relatively different degree of distortion at low processing temperature. At low temperature, the surface is not as smooth as in the case of samples processed at high temperature. These extrudates in fact have rough, irregular surfaces, loss of glossiness and non-uniform diameter. This is due to the melt fracture that occurs in the elastically deformed polymer, in which the shear stress exceeds the strength of the melt. The extensive slipping and sticking of the polymer layer at the wall of the capillary is also one of the factors that contribute towards extrudate deformation (Georgiou, 2004; Rahimb et al, 2011).

Apart from causing extrudate distortion, flow instability for PP may also manifest in other ways such as blisters are formed on the surface of the extrudates and void in the cross section of the extrudates as shown in Fig. 11 obtained at the temperature of 210°C for PP-kaolin composites using a single-screw extruder. The first reason is that as more kaolin was incorporated inside the matrix, the activation energy barrier was reduced due to the particle-molecule interface which led to increasing number of nucleation sites and was able to increase the nucleation rate. Consequently, less force was required to overcome the activation energy barrier, resulting in the formation of more bubbles on the extrudate surface. Whereas for the second reason is due to the melt suddenly goes from high pressure to atmospheric pressure during the emergence of extrudate of the die exit and then undergo a sudden quench in cool water that provided a large temperature gradient (Rahima et al., 2011; Rahim, 2010).



Void in PP-kaolin composites extrudates cross section

Bubble formations on PP-kaolin composites surface

Fig. 11. Flow instabilities for PP-kaolin composites using single screw extruder at 210°C

The extensional flow along the melt will cause an orientation to the polymer chains. Solidification through this type of process condition is favorable for residual stress formation which is one of the factors that can cause shrinkage in many polymer products and in this case, the extrudates. The polymer will freeze the surface in this orientation direction and in the meantime, the flow between the solid layer is affected by the temperature gradient resulting in unbalanced cooling where the inner layer cools slowly with respect to the skin layer. As mentioned previously, after exiting the die, the composites will swell first then followed by cooling. Thereby after quenching, the surface layer of the extrudates will solidify first while the inner layer is still in a molten stage. Soon after, as the inner melted layer cools down, it will be attracted to the cooled skin of the extrudate layer. Thus, a void is created in the composites extrudate since the total composites volume reduces with time as the temperature gradient drops (Rahim^a et al, 2011; Rahim^b et al., 2011).

5. Conclusion

Overall, the rheological properties of PP are highly dictated by its molecular structure. The chain configuration of the methyl group placement will create different tacticity for PP and subsequently leads to different rheological characteristics. Another contributing factor is the presence of ethylene group such found in some PP copolymers which may increase the flowability of the resin during processing as forwarded in the preceding sections. Besides these internal factors, externally, the rheological behaviour of PP is highly influenced by additives, which are either added to modify the properties of the base compound or for the ease of processability. Incorporation of fillers normally creates higher viscosity of PP melts compared to the pure PP matrix. Whereas, the incorporation of plasticizers, compatibilizers, degradation promoters and incompatible components in the PP blends can correspondingly caused a decreasing trend of viscosity.

Capillary rheometry and extrusion have shown significant importance in measuring rheological behaviour of polymers. As for PP, the above forwarded discussion has proven that its rheological behaviour can be evaluated successfully with both instruments. Our

study also proved that both instruments are able to reveal viscoelastic responses of PP melt such as extrudate swell and several types of flow instabilities which cannot be investigated with other types of rheological instrument. The extrudate swell behaviour is caused by a number of factors such as temperature, L/D ratio of the die, flow geometry, filler loading which are eventually connected to the memory effect of the PP melt. Various types of flow instabilities can be observed through capillary rheometry and extrusion process; from periodic extrudate distortion to severe melt fracture. Flow instabilities may also be revealed as loss of glossiness, formation of blistered extrudate surface and even formation of void within the extrudate cross section. These flow instabilities are triggered whenever processing conditions are not optimized and/or exceeded the elastic limit of the PP melt which can be controlled via several approaches such as incorporation of fillers, increasing the die L/D ratio and incorporation of suitable flow promoter.

6. References

- Andres, J. A., Pena, B., Benavente, R., Perez, E., Carrada, M. L. (2007). Influence of isotacticity and molecular weight on the properties of metallocenic isotactic polypropylene. *Eur. Polym. J.*, 43, 2357-2370
- Ariff, Z. M. (2003). Melt rheology and injection moulding of acrylonitrile-butadiene-styrene (ABS) using a capillary rheometer. *Phd Thesis*, Universiti Sains Malaysia
- Ariffin, A., Mansor, A.S., Ariff, Z. M., Jikan, S.S., Ishak, Z.A.M. (2008). Effect of filler treatments on rheological behaviour of calcium carbonate and talc-filled polypropylene hybrid composites *J. Appl. Polym. Sci*, 108, 3901-3916
- Ariffin, A., Jikan, S. S., Samsudin, M. S. F., Ariff, Z. M., Ishak, Z. A. M. (2006). Melt elasticity phenomenon of multicomponent (talc and calcium carbonate) filled polypropylene. *J. Reinf. Plas. Compos.*, 25, 913-923
- Ariffin, A., Ariff, Z. M., Jikan, S. S. (2011). Evaluation on extrudate swell and melt fracture of polypropylene/kaolin composites at high shear stress. *J. Reinf. Plas. Compos.*, 30, 609-619
- Azizi, H., Ghasemi, I., Karrabi, M. (2008). Controlled-peroxide degradation of polypropylene: rheological properties and prediction of MWD from rheological data. *Polym. Test.*, 27, 548-554
- Berzin, F., Vergnes, B., Delamare, L. (2001). Rheological behavior of controlled-rheology polypropylenes obtained by peroxide-promoted degradation during extrusion: Comparison between homopolymer and copolymer. *J. Appl. Polym. Sci*, 80, 1243-1252
- Brydson J.A. (1970). *Flow Properties of Polymer Melts*. London; Iliffe Books.
- Cogswell, N. (1981) *Polymer melt rheology: A guide for industrial practice*. Woodhead Publishing Limited.
- Georgiou, G. (2004) Stick-Slip Instability. *Polymer Processing Instabilities: Control and Understanding*. Marcel Dekker, New York.
- Gonzales, V. A., Velazquez, G. N., Sanchez, J. L. A. (1998). Polypropylene chain scissions and molecular weight changes in multiple extrusions. *Polym. Degrad. Stab.*, 60, 33-42
- Gotsis, A. D., Zeevenhoven, B. L. F., Tsenoglou, C. (2004). Effect of long branches on the rheological behaviour of polypropylene. *J. Rheo.* 48, 895-914
- Gupta, R.K. (2000). *Polymer and Composite Rheology*. Marcel Dekker Inc. New York
- Han C. D. (1976). *Rheology in Polymer Processing*. Academic Press. New York

- Hingmann, R., Marczinke, B. L. (1994). Shear and elongational flow properties of polypropylene melts. *J. Rheo.* 39, 573-588
- Jikan, S. S., Samsudin, M. S. F., Ariff, Z. M., Ishak, Z. A. M., Ariffin, A. (2009). Relationship of rheological study with morphological characteristics of multicomponent (talc and calcium carbonate) filled polypropylene hybrid composites. *J. Reinf. Plast. Compos.* 28, 2577-2587
- Jikan S. S. (2010). Evaluation on flow behaviour of polypropylene/kaolin composites at high shear stress. *Phd Thesis*, Universiti Sains Malaysia.
- Jikan, S. S., Ariff, Z. M., Ariffin, A. (2010). Influence of filler content and processing parameter on the crystallization behaviour of PP/kaolin composites. *J. Therm. Anal. Calorm.*, 102, 1011-1017
- Karger-Kocsis J. (1995) *Polypropylene: structure and morphology*. Chapman and Hall, Cambridge.
- Keawwattana, W. (2002). Phase behaviour, crystallization and morphological development in blends of polypropylene (PP) isomers and poly(ethylene-octane) copolymer. *Phd Thesis*. University of Akron.
- Liang, J. Z. (2001). Pressure effect of viscosity for polymer fluids in die flow. *Polym.*, 42, 3709-3712
- Liang J. Z., Ness J. N. (1998). The melt die-swell behaviour during capillary extrusion of LDPE/PP blends. *Polym. Test.*, 17, 179-189
- Liang, J. Z. (2008) Effects of extrusion conditions on die-swell behavior of polypropylene/diatomite composite melts. *Polym. Test.*, 27, 936-940.
- Liang, J. Z. (2002) The Melt Elastic Behaviour of Polypropylene/Glass Bead Composites in Capillary Flow. *Polym. Test*, 21, 927-931.
- Liaw, W. C., Huang, P. C., Chen, C. S., Lo, L. C., Chang J. L. (2008). PPgMA/APTS compound coupling compatibilizer in PP/Clay hybrid nanocomposites. *J. Appl. Polym. Sci.*, 109, 1871-1880
- Maiti, S. N., Singth, G., Ibrahim, M. N. (2003). Rheological properties of calcium silicate-filled isotactic polypropylene. *J. Apply. Polym. Sci.*, 8, 1511-1518
- Muksing, N., Nithitanakul, M., Grady, B. P., Magaraphan, R. (2008). Melt rheology and extrudate swell of organobentonite-filled polypropylene nanocomposites. *Polym. Test.*, 27, 470-479
- Micheali, W. (1992). *Extrusion dies for plastic and rubber: design and engineering*. Munich. Hanser Publishers.
- Ogawa, T. 1992. Effect of molecular weight on mechanical properties of polypropylene. *J. Appl. Polym. Sci*, 31, 1151-1154
- Osswald, T.A. (1998) *Polymer processing fundamentals*. Munich. Carls Hanser Verlag.
- Prentice, P. (1997). *Rheology and its role in plastics processing*, Vol 7, Rapra Technology Limited, United Kingdom.
- Rahim N. A. (2010). Flow behaviour and viscoelastic properties of polypropylene-kaolin composites. *MSc Thesis*, Universiti Sains Malaysia.
- Rahim,^a N. A. A., Ariff, Z. M., Ariffin, A. and Jikan, S. S. (2011). A study on the effect of filler loading on flow and viscoelastic behavior of polypropylene/kaolin composites. *J. Appl. Polym. Sci.*, 119, 73-83
- Rahim^b, N. A. A., Ariff, Z. M., Ariffin, A. (2011). Flow behaviour and viscoelasticity of polypropylene-kaolin extruded composites at different temperatures. *Pertanika J. Sci. & Technol.* 19, 383-388

- Rothon, R.N. (2003) *Particulate-filled polymer composites*. Rapra Technology Limited, United Kingdom.
- Samsudin, M. S. F., Ishak, Z. A. M., Jikan, S. S., Ariff, Z. M., Ariffin, A. (2006). Effect of filler treatment on rheological behaviour of calcium carbonate and talc-filled polypropylene hybrid composites. *J. Appl. Polym. Sci*, 102, 5421-5426.
- Scheirs, J. (2000). *Compositional and Failure Analysis of Polymers*. England: John Wiley & Sons, Ltd.
- Song, N., Zhu, L., Yan, X., Xu, Y., Xu, X. (2008). Effect of blend composition on the rheology property of polypropylene/poly (ethylene-1-octene) blends. *J. Mater. Sci.*, 43, 3218-3222.
- Shenoy, A.V., Saini, D.R. (1996) *Thermoplastic melt rheology and processing*. Marcel Dekker, Inc., New York.
- Tanaka, H., White, J. L. (1980) Experimental investigations of shear and elongational flow properties of polystyrene melts reinforced with calcium carbonate, titanium dioxide and carbon black. *Polym Eng. Sci*, 20, 946-956.
- Thitithammawong, A., Nakason, C., Sahakaro, K., Noordermer., J. (2007). Effect of different type of peroxide on rheological, mechanical, and morphological properties of thermoplastic based vulcanizates based on natural rubber/ polypropylene blends. *Polym. Test.*, 26, 537-546
- Wen, S. H., Liu, T. J., Tsou, J. D. (1994). Three-dimensional finite element analysis of polymeric fluid flow in an extrusion die. Part I: Entrance effect. *Polym. Eng. Sci.*, 14, 212-222
- White, J. L. (1973). Critique on flow patterns in polymer fluids at the entrance of a die and instabilities leading to extrudate distortion. *Appl. Polym. Symp*, 20, 155-174.
- Yu, Y. W., Wu, P. V., Liu, T. J. (1997). Validity of one-dimensional equation governing extrusion die flow. *AIChE Journal*, 43, 3117-3120