SLIT DIE RHEOLOGY OF HDPE AND ABS BASED WOOD PLASTIC COMPOSITES

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Abstract

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As the use of wood plastic composite materials has continued to increase, the research into the rheology of these materials has taken a back seat to the characterization of the mechanical properties. However, for an accurate determination of the mechanical properties to occur, an understanding of the rheological behavior of the melt is needed, since changes in the melt can directly affect the final product properties. A rheological slit die was used to quantify the shear viscosity, shear stress and extruder motor current for acrylonitrile-butadiene-styrene (ABS)/ and high-density polyethylene (HDPE)/wood filled melts. Using a Carreau curve fit, the viscosity results indicate that there is a significant increase in the melt viscosity as the wood filler amount increased. In HDPE melts, when the wood filler size and wood species changed, there was little observed change in the viscosity. With the ABS based melts, when the temperature of the melt increased, the shear viscosity of the melt decreased. This change in melt temperature was then used to create master curves by reducing the viscosity and shear rate. Since the shifting factors used to create the master curves followed an Arrhenius curve fit, the melt activation energy of the ABS melts was also determined. In both the ABS and HDPE melts, the melt shear stress increased as the temperature decreased and the wood filler content increased. Similar trends were observed when the required motor current load was analyzed for the HDPE melts, but there was more variation in the data as compared to the observed shear stress and viscosity results.

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CHAPTER 1 - INTRODUCTION

1.1 Background

Wood plastic composites (WPC) composed of wood and either a thermoplastic or thermoset resin have existed since the early 1900's (Clemons, 2002). However, the development of these WPC in the United States did not really begin to gain momentum until several decades ago. During the late 1990's the production of WPC increased four-fold and by 2001 the annual production was around 700 million tons (Li, 2004; Clemons, 2002). More recently, WPCs have found an expanding market in the residential building industry, due to an increased amount of available applications. The most common WPC formulations are comprised of a thermoplastic matrix filled with. The three most common thermoplastics used by the WPC industry are polyethylene (PE), polypropylene (PP) and polyvinylchloride (PVC).

In 1999, the three polymer resins of PE, PVC and PP resins accounted for approximately 70%, 17%, 13%, respectively, of the total WPC production (Patterson, 2001). Each one of these resins has its own advantages and disadvantages when combined with the wood filler. PE based WPC tend to have higher heat resistance and are less expensive then comparable PVC formulations, while PVC based WPC offer increased stain and paint ability (Patterson, 2001). However, one of the biggest disadvantages of WPC, no matter which resin is used, is that they tend to be heavier than the traditional timber products they replace.

Therefore, one of the major focuses within the WPC industry is reducing the weight of the composites through the use of chemical foaming agents (Schut, 2001). As WPC foaming production increases, manufacturers are expanding on the different types of polymers used in their production. Some of the newest types of polymer resins used in WPC products are the amorphous resins of polystyrene (PS), acrylonitrile-styrene-butadiene (ABS), and styrene-acrylonitrile (SAN). These polymers lead to a stiffer foamed WPC, but it is believed that is mainly due to a reduction in the amount of wood fiber used in the composite (Schut, 2001).

Most WPC products are manufactured by using either a single or twin-screw extruder. The extruder uses the pressure developed by the rotating screw flights to push the molten mixture through a die. Once the extrudate exits the die, it is cooled in a water spray bath and a shaped composite is formed. Most WPC are formulated with about 50 wt% wood flour, but this number can be as low as 10 wt% and as high as 70 wt% (Kowalska, 2001). To this wood and polymer mixture, the manufacturer will add their selected fillers, modifiers and additives to produce the desired final formulation. Therefore, the importance of understanding the interactions of these individual components within the extrudate melt and their effects on the overall melt behavior, is an important area of research that needs more investigation (Shah, 2004).

1.2 Significance

Within the WPC community, most of the research is aimed at answering questions related to the mechanical properties of the final product. While quantifying this aspect of WPC behavior is important, little research has been done in relation to understanding the melt properties. This poses a serious problem, since the choice of correct formulation, process-ability of the formulation and extruder die designs are based off an understanding of these flow properties. Since commercial WPC formulations typically involve high wood loading amounts, and a variety of additives, lubricants and modifiers, the ability to draw conclusions from other types of filled polymer systems is very limited (Li, 2005). As the industry continues to grow, the need to better understand the rheology of these systems will play an even more important role in the development of new WPC products. By quantifying these properties correctly, the industry will be able to increase production and develop the necessary products to meet the expected growth.

Most previous work on WPC rheology has been conducted on a capillary die rheometer (Li, 2004; Li, 2005; Guffey, 2002). The theory behind this method is well developed and has already been proven useful for rheological studies of WPC and other highly filled polymer systems. However, the use of an off-line capillary rheometer faces some major drawbacks when testing WPC systems. Formulations comprised of ABS, PVC and other heat sensitive polymers cannot easily be used since the melt is subjected to extended periods of high temperatures. Secondly, the simulation of the actual flow conditions seen in actual production is not accurately represented in off-line techniques. Therefore, a better-suited rheometer for the measurement of rheological properties of the melt is an on-line slit die rheometer. This rheometer uses a theory that is very similar to the capillary rheometer to obtain the rheological data, but allows for a wider variety of formulations to be analyzed.

1.3 Objectives

This research project investigates the rheological properties of wood-plastic composite (WPC) melts by means of a slit die rheometer. The conventional capillary die method presents a problem when working with thermally sensitive melts due to the extended dell times at elevated temperatures. It is also known that the offline capillary die method is subject to size effect problems with filled melts, and does not represent the actual melt flow conditions seen during extrusion from the die. The slit die rheometer overcomes these problems, as well as determines the shear viscosity, shear stress and motor current of the melt. The specific objectives of this research are as follow:

1. Develop a technique to accurately measure the rheological properties of different WPC melts using an in-line slit die.
2. Compare the HDPE/wood slit die shear viscosity values to published capillary die results.
3. Established the effects of wood filler amount, particle size and species on the shear stress and motor current in HDPE melts, and
4. Examine the changes in the rheological properties of ABS/maple melts, as the wood filler percentage, melt temperature and the level of SAN is varied.

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CHAPTER 2 – HDPE/WOOD COMPOSITE RHEOLOGY

2.1 Abstract

In the last decade, wood-plastic composites (WPCs) have emerged as a viable replacement to many traditional timber products used in the residential construction industry. While most WPC research deals with the mechanical properties of these products, little research has gone into understanding the flow mechanisms of WPC in production. As the subsequent production of WPC has increased, the need to better understand the rheological behavior of the melt has become an important concern, since changes in the rheological properties can alter the overall product shape and mechanical properties of the composite. In this work, the rheological properties of high-density polyethylene (HDPE) filled with either maple or pine wood flour were studied with a specially designed slit die. Melt viscosity was found to increase with wood filler content and decrease with shear rate. Changes in the wood mesh size and species were determined to have little effect on the viscosity of the melt. When these results were compared to identical formulations run using standard capillary die techniques, the slit die viscosity results were up to 62.5% lower. This difference may be attributed to differences in processing conditions and die sizes between the two dies. Besides using the slit die to determine the viscosity of the melt, the shear stress and extruder current were also determined. Almost identical trends to the shear viscosity results were observed in the shear stress and extruder motor. This information provides vital information for the WPC manufacturer and allows for a better final product to be produced.

2.2 Introduction

The market for wood plastic composites (WPC) has continued to grow over the past two decades with 700 million lbs. of WPCs being manufactured in 2001 (Mapleston, 2001). These materials are composed of organic filler with a polymer matrix. As WPCs have become more accepted they have expanded into a wider variety of applications. The most growth has occurred in the residential building market as composite deck boards, siding and window moldings are being used as replacements to traditional timber products.

While these composites can be manufactured with a variety of thermoplastic resins, the use of high-density polyethylene (HDPE) continues to dominate commercial products (Clemons, 2002). A 50% wood filler amount is commonly used in HDPE-based WPC (Li and Wolcott, 2005). These composites are defined by good mechanical properties and lower material cost, due to the high percentage of wood filler (Kowalska and Pelka, 2001). The wood filler adds strength and provides rigidity to the polymer matrix, while improving processing, machining properties, and material costs.

To correctly design a formulation, the melt rheology of the composite must be assessed. While undertaking rheological tests, the processor attempts to solve two common extrusion problems. First, the amount of required empirical testing is reduced, because the slit or capillary die used to determine the rheology can simulate die flow conditions (Glomsaker et al., 1999). Secondly, the consequential modifications to the original die design are reduced through greater understanding of melt rheology.

While most rheological studies of WPC formulations are conducted using off-line capillary die rheometry (Li and Wolcott, 2004, 2005; Guffey and Sabbagh, 2002), the use of on-line slit die rheometry to test the rheological properties of these materials avoids some inherent disadvantages prevalent in the capillary die methods. Two major problems are commonly encountered when using an off-line capillary rheometer. The first problem is that formulations comprised of heat sensitive polymers and fillers cannot easily be tested due to the extended dwell time at elevated temperatures required for off-line techniques. Secondly, an off-line capillary rheometer does not represent the actual flow conditions encountered by the melt as it is extruded from the die. While providing an improved simulation of melt flow, an on-line rheometer simulates the particle migration and orientation within the melt better than off-line techniques (Thorsteinsen, 2003).

To overcome WPCs testing problems in off-line capillary die rheometry, an on-line slit die rheometer is used to quantify the important melt flow characteristics. This will involve determining the viscosity, shear rate, and shear stress for a variety of HDPE/wood composite blends. A technique will be developed to accurately measure the rheological properties of different WPC formulations in the melt state. This technique will then be used to compare the rheological values obtained for variety of HDPE/wood composites using the slit die, to published values obtained from capillary die methods.

2.3 Literature Review

2.3.1 Slit Die Rheology

Slit dies have been used extensively to measure rheological properties of unfilled polymer melts (Han 1971, 1974). Based on the unfilled polymeric systems Han investigated, no difference appeared in exit pressure results between the slit die and capillary die results. When examining the viscosity flow curves for the melts, the results obtained with slit and capillary die strongly correlated.

Many of the equations used in slit die analysis are based on the work of Han (1971, 1974), Eswaran (1963) and Wales (1965). The theoretical concepts and equations behind the slit and capillary die are the same, with the main differences occurring in the channel geometry (i.e. rectangular vs. circular).

For accurate results using a slit die, a minimum of three pressure transducers are required along the land length of the die. Knowing the pressure gradient along the longitudinal length axis ($-\partial p / \partial x$), the shear stress and shear viscosity can be obtained. However, the equations for the slit die are more complicated than the capillary dies and are based on rectangular Cartesian coordinates. A full derivation of these equations are found elsewhere (Han 1974), but a brief synopsis is presented. Accordingly, the shear stress at the die wall (τ_w) in a rectangular channel is given as:

$$\tau_w = \left(\frac{\partial p}{\partial x} \right) \frac{h}{2} \tag{1}$$

where *h* is given as the slit height. The apparent shear rate ($\dot{\gamma}_a$) in the melt is defined by:

$$\dot{\gamma}_a = \frac{6Q}{wh^2} \tag{2}$$

where w is the width of the slit die, and Q is the volumetric flow rate. The theoretical conversion of $\dot{\gamma}_a$ to obtain the true shear rate ($\dot{\gamma}$) as developed by Han is expressed as:

$$\dot{\gamma} = \left(\frac{2n+1}{3n} \right) \dot{\gamma}_a \tag{3}$$

where n is the Rabinowitsch correction factor (n=$d \log \tau_w / d \log \dot{\gamma}_a$) for shear thinning melts or a power law (n=1) for Newtonian melts. Note that this derivative is calculated by testing at least two different shear rates for each formulation (Laun, 1983).

2.3.2 Comparison of slit and capillary die rheometry

While the use of a capillary rheometer to determine the rheological properties of a variety of different filled and unfilled polymers has been well proven, the application of slit die rheometry are more limited. The advantages of capillary rheometry lie in the well-developed analysis of the simple flow behavior. However, the most significant disadvantage is the fact that the cylindrical chamber prevents flush mounting of the perpendicular pressure transducer. Therefore, the curvature of the cylindrical die produces a gap between the edge of the transducer tip and the die wall. This small gap creates a disturbance in the shear flow around the hole, thus inducing a potential source of error termed the "pressure hole effect" (Walters, 1975; Han, 1980). Unlike the capillary die, the slit die (Figure 2.1) is perfectly flat allowing the mounted pressure transducer to lie flush with the die surface and eliminating any possible "hole effect". This geometry facilitates a more accurate measurement of the melt pressure (McGinnis and Han, 1978; Macosko, 1994). Despite the fact that others found the pressure hole effect to be negligible for unfilled polymers (Han, 1972), the influence of such a flow disturbance is suspect when evaluating WPCs. Similar asperities in dies tend to produce charred inclusions that grow with time as the thermally sensitive natural fibers degrade.

When the capillary rheometer is used to determine the rheological properties of WPC melts, a variety of other problems can be encountered. When these materials are used in a capillary die rheometer, the particle size of the wood filler is governed by the exit hole size. This constraint limits the analysis to small particle sizing. In addition, since wood fibers are anisometric (aspect ratio of ~10), the constrained flow of capillary dies produce oriented material structures that may not exist in other configurations. The large exit opening of the slit die geometry reduces some of the particle size problems. To meet the continuum requirements assumed in design, the minimum dimension of the die should be 40 times larger than the average filler particle size found in the melt.

Unlike traditional batch capillary rheometers where long soak times are required to fully develop die flow, the slit die method is a continuous process. This attribute is especially important for formulations where thermally sensitive matrix resins are blended with thermally sensitive wood. Polyvinyl chloride exposures to high temperatures can lead to a thermal instability within the resin and the release of toxic HCL (Penn, 1969). In the case of acrylonitrile-butadiene-styrene (ABS), this extended temperature exposure can lead to depolymerization, reducing both molecular weight and mechanical properties of the final product (Tiganis et al., 2002).

Despite several positives of the slit die, there are some potential negatives to be minimized during testing. Since the die is mounted directly onto the screw extruder, there are many variables affecting material flow rate (i.e. screw speed, multiple barrel and die temperature controllers, feed rate, etc.) that must be monitored. Also, the slit die must be completely dismantled for cleaning after each run. This is especially important to facilitate calibration of the pressure transducers at the beginning of each test (Macosko, 1994).

2.3.3 Slit Die Design

For the flow of the material within the slit die to be considered one-dimensional, the slit must have a constant height-to-width ratio that is equal to or greater than 1:10 (Han, 1971). This condition satisfies the assumption that the flow in the slit is acting as a set of infinite parallel plates, thereby allowing edge effects to be neglected (Han, 1976). Based on the designed height of 5.0-mm and the requirements for flow that is free of edge effects, the slit width was designed at 50.0-mm.

Another important aspect in the design of the slit die is the location of the pressure transducers. Most importantly, the first transducer must provide sufficient distance from the die entrance to fully develop flow. Han (1971) used flow birefringment techniques to show that a minimum of 3-4 times the slit height is needed for this length. For our slit die with a 5.0-mm slit height, a 20.0-mm minimum distance between the end of the transition and the first transducer was required. To ensure a fully developed flow of the highly filled melt, the first pressure transducer was placed 50.0-mm downstream from the entrance of the slit. The remaining two transducers were located at 37.5-mm intervals.

This slit die design was developed around the principles of continuum flow with a maximum wood flour particle width of 0.0635-cm (40-mesh). If this requirement is not satisfied, the melt cannot be considered homogenous, but instead it is considered a multi-phase flow. To validate the continuum assumptions used in the die design, the particle size of the dispersed wood filler was analyzed *in-situ* using a scanning electron microscope (SEM) (Hitachi S-570).

The SEM method is preferred over a simple measurement of particle sizes because the sieve analysis fails to consider important processing aspects. Since the sieve analysis is completed before processing, it does not take into account what is happening to the filler within the melt during processing. The processing steps found within extrusion can have profound affects on the filler materials, such as, a breakage of the fibers due to the rotating flights of the extruder screws. George et. al (1996) has shown that PE filled with pineapple fiber has an increased amount of fiber breakage when the shear rate is increased. When compared to the pre-extrusion length, the average length of the pineapple fibers was reduced by 21.7% at a shear rate of $16.4s^{-1}$. Fiber breakage is not the only change that affects the particle size. Wood filler amount within the melt will also alter the size of the wood filler. Stark and Berger (1997) found that the high pressures of WPC extrusion can cause the cells of wood flour to collapse. This collapse leads to a reduction in the particle size.

To conduct the SEM measurements, a representative slit die extrudate containing 60% 40-mesh maple and 40% HDPE was randomly sampled and milled into two 5-mm cubes. A diamond microtone was then used to surface the cubes on one face normal to the flow direction. Each sample was sputtered with a 6.0-Å thick gold layer prior to examining. A series of forty SEM pictures were acquired over the two samples using a magnification of 490x. The magnification was selected to balance edge detection of the wood particles and field of view. A total of 150 points were analyzed to determine the particle heights at given points in the SEM picture. Since every picture was 1200 pixels wide by 1500 pixels high, ten random x-y coordinates within these ranges were assigned for each picture. These points were constant throughout the 15 randomly chosen pictures. At each one of these x-y coordinates the height of the particle was measured using image analysis software (UTHSCSA ImageTool). The same calibration length was used for all of the pictures since the magnification of the images was constant throughout. After measuring the particle height, it was determined that 136 points contained a particle, while 14 points did not.

2.4 Materials

The rheometry was performed using HDPE filled with between 30 and 70 wt% wood flour. The wood flour filler was commercially obtained (American Wood Fibers) as either maple (*Acer spp.*) or pine (*Pinus spp.*) in the mesh sizes ranging from 40 to 100. Prior to extrusion, the wood flour moisture content was reduced from 8.0% (as received) to < 3.0%, in an open-ended extruder (Cincinnati Milicron TC 86) set at 190°C and a screw speed of 25-rpm. The HDPE reactor flake (Equistar LB-0100-00, MFI = 0.1 g/10 min, MW=91.6 kg/mol) was used as received. All formulations were dry blended in 1.2-m drum tumbler for 10-min. prior to extrusion to assure a proper dispersion of the components. A complete listing of the formulations used in this research is found in Table 2.1.

2.5 Methodology

2.5.1 Slit Die Setup

Following thorough cleaning, to remove damage remnants of material, the slit die was mounted to a twin-screw conical counter rotating extruder (Cincinnati Milicron CM35). Three pressure transducers (MPI MTJ07P7.5MSS, MPI MPJ07P5MSS, and

Dynisco TPT4636-7.5M-6/18) were mounted flush along the lower slit die wall (Han, 1974; Laun, 1983). Each transducer is shunt calibrated and data was digitally acquired during the extrusion runs. Each of four die zones were equipped with separate band or plate heaters and type J thermocouple that were attached to the control system of the extruder. During extrusion runs, the temperatures of the die and the extruder zones were controlled to the same temperature at ± 2.0-degrees.

2.5.2 Slit Die Measurements

Thorsteinsen et. al (2003) and Martin et. al (2003) observed that when the melt is being extruded, the pressures vary during the initial startup phase of the extrusion where data collection is unadvisable. This period may last between 2 and 20 minutes depending on the system under study after which data is sampled at a rate of 1-Hz. The collected data set is comprised of 15 readings for each of the three transducers. This process is repeated twice over the next two minutes. During the second sampling period, a sixty-second physical sample is collected by cutting and loosely folding a timed section of extrudate at the die exit. This method is similar to one used by others (Thorsteinsen et. al. 2003). The physical sample is used to compute the mass flow rate of the extruder (Chastagner, 2005a). This parameter was converted to the volumetric flow rate (Q) using the density of the extrudate as determined using ASTM D-2395.

2.6 Results

2.6.1 Particle Size Analysis

The distribution of particle heights (Figure 2.2) measured in the extrusion cross-section follows a lognormal distribution type as verified using a Kolmogorov-Smirnov

(K-S) goodness of fit test with a β=0.05 (Chastagner 2005b). Therefore, the mean particle height ($\bar{x}$) may be determined by first transforming the individual height data (x_i) using:

$$y_i = \ln x_i \tag{4}$$

and then computing the average as:

$$\bar{x} = e^{\bar{y}} = e^{\sum y_i/n} \tag{5}$$

where n = total number of samples. This resulted in an average particle height of 25.6 μm. To validate the slit height for continuum assumptions, the mean particle height is multiplied by 40 to yield a minimum die height of 1.02-mm. This value is well below the 5.0-mm slit height and does not violate the continuum requirements.

2.6.2 Comparison of capillary and slit die results

While most of the literature related to the rheology of WPCs is based on capillary die results, a small amount of research has been completed on slit die rheology. Therefore, there is a strong need to validate both the design of the slit die and the methodology for use on WPCs. All of the formulations provided in Table 2.1 have been previously characterized using capillary rheology (Li and Wolcott, 2004, 2005). By comparing the results obtained in this slit die research with the published results of Li and Wolcott, the validity of the slit die for WPC rheology will be determined.

The Carreau (Carreau et al., 1996) equation was used as a constitutive relation for all formulations:

$$\frac{\eta-\eta_\infty}{\eta_0-\eta_\infty}\approx\frac{\eta}{\eta_0}\approx\frac{1}{\left[1+\left(\lambda\dot{\gamma}\right)^2\right]^{\frac{1-n}{2}}} \tag{7}$$

where n and λ are curve fitting parameters, and η_∞ and η_o are the viscosity at infinite and zero shear rate, respectively. While a vast majority of the shear viscosity data appears to be linear when plotted on a log-log plot, if a complete shear rate spectrum was examined, it is expected that the data would not follow this trend. In most polymeric systems, a flat plateau in viscosity is observed at lower shear rates. Then the viscosity reduces downward into a power-law fitting region. Afterwards, the shear rate increases and the slope levels off again. Li and Wolcott (2004) observed this change in viscosity when they examined WPC filled melts in a capillary rheometer. Therefore, the Carreau fit was chosen because it can predict the leveling off of the viscosity at both the high and low shear rate values. The power law cannot predict the results accurately since it is limited to the linear viscosity results. The Carreau fit also allows for the determination of a predicted η_o value.

A comparison of the power law and Carreau curve fits are shown in 2.3. Both fits approximated the linear results of the 70% maple formulation equally well. However, the Carreau model captured the slight nonlinearity of the 30% maple formulations with better accuracy. The appearance is validated by the R^2 values for the power law and Carreau model of 0.787 and 0.837, respectively. In comparison, for the 70% formulation, the R^2 values are 0.857 for the power law and 0.858 for the Carreau model. Therefore, not only does the Carreau model give a better fit for the data over the entire shear rate range, but it also provides a better fit for the linear-like regions of these two formulations as well.

Based on this, the Carreau model will be used throughout this analysis. The Carreau parameters for all formulations are presented in Table 2.2. Figure 2.3 shows a typical flow curve collected from the slit die and the Carreau curve fitting applied to that data. Because the shear rate of the melt cannot be absolutely controlled with this slit die setup, most of the points tend to congregate around a general shear rate value. This figure, along with other melt flow curves, contains three separate runs of each formulation. However, in the interest of clarity, only the Carreau curve fit will be plotted for all of the figures.

2.6.3 Shear Viscosity

A predominate shear thinning behavior is observed for both the pine and maple formulations tested. Other researchers have also observed this behavior when conducting research on WPCs (Li and Wolcott, 2004, 2005; Guffey and Sabbagh, 2002; Shah and Matuana, 2004). However, the degree of shear thinning appears to vary depending on the composition of the formulation.

A variety of formulations using 40-mesh maple in HDPE-wood formulations were examined and are shown in Figure 2.4. The wood filler content varied from 30 to 70% wood content. As the percentage of wood filler in the melt increased, the viscosity of the melt increased and can be attributed to an increased bridging between the wood particles contained within the melt. This behavior is comparable with results found by other authors for both HDPE-wood systems (Li and Wolcott, 2005) and other highly filled plastics (Vlachopoulos and Strutt, 2003; Han, 1974b). It is also important to note that with the lower wood content levels (30%) there is a plateau behavior occurring within the viscosity results. This behavior can be attributed to the orientation of the suspended wood filler within the melt and the shear rate of the test. At the shear rates tested, the higher wood filler percentage melts already begin to exhibit shear thinning behavior. This effect is due to the concentration of macromolecular entanglements within the melt decreasing (Mayadunne et. al, 1996). At the decreased wood filler amounts, with lower shear rates, the molecular segments are well entangled and the melt is exhibiting a Newtonian behavior and is still within the level plateau region.

Although, the melt viscosities of high filler ratios were similar to those determined using capillary rheometry, this agreement deteriorates with decreasing wood loadings. For instance, the viscosity of 30% maple-HDPE composites nearly 62% lower with the slit die configuration than when tested using a capillary rheometer. This difference is easily seen in Figure 2.5 and this deviation in viscosity may be attributed to the differences in the methods of the two different rheometers. Prolonged exposure to an elevated temperature in the capillary die causes a relaxation of the pre-shearing effects. While in the slit die the melt is continually being extruded and the pre-shearing effects are not minimized (Mutel and Kamal, 1991). Since the slit die has an exit opening that is considerably larger in size than the capillary die, it is expected that the orientation of the fibers at lower filler amounts will be more random than in the capillary die. Therefore, at lower filler levels, the melt flow between the two methods will be different. The slit die has a particle orientation history that affects the flow, while the capillary will be free of this constraint. This orientation history leads to a difference in the melt shear viscosity between the two methods at lower filler levels. As the amount of filler within the melt increases, the effect of the die dimensions on particle orientation become stronger. Li and Wolcott (2004) have indicated that as the filler level reaches 40 to 60%, maple based melts have an increasing dependence on die geometry. In the case of higher filler levels, the random orientation of the particles within the melt will be decreased and the deviations in the shear viscosity between the two different will be reduced.

It is common for different rheometers to produce different shear viscosities when geometric differences exist in the flow channel (Glomsaker et al., 1999). It is also important to note that when the preparing the samples for the capillary die results by Li and Wolcott (2005), the materials were pre-compounded, a step not found in the slit die tests. Therefore, the shear flow history of the two samples is different, potentially leading to a difference in the morphology of the melts (Han et al., 1995). Using two different rheometers, Han showed that for single-phase flows, there is overlap between the shear viscosity results. However, for multiphase flows, the melt morphology changes can greatly alter the shear viscosity results. This observed deviation in the slit and capillary die results may indicate that these melts are multiphase flows. Neither this work nor the capillary results achieved by Li and Wolcott accounted for this type of flow, therefore further work is required to determine if this is the reason for the deviation between the slit and capillary die results.

Besides a change in viscosity due to different filler percentages, a weak dependence on the mesh size of the wood filler was found. Figure 2.6 shows that for a 40% maple loading, an increased maple mesh size decreased the overall melt viscosity slightly. This phenomenon results from a decreased bridging in the smaller particle size, allowing for slippage of nearby particles as the melt is sheared. Similar results were also found in capillary die rheology conducted by Li and Wolcott (2005).

Li and Wolcott (2004) reported differences in viscosity between pine and maple wood flours in HDPE/wood composites. The results obtained by the slit die method indicate that both maple and pine exhibit different viscosities with changes in wood filler percentage. Both wood species follow the same trend, in that the 60% filler level produces a higher viscosity than the 40% filler level.

Upon caparison to the capillary rheology (Li and Wolcott 2004), it appears that the slit die similar trends in the case of maple-based composites. However, the results of the pine formulations are in stronger disagreement. Li and Wolcott's work indicated that there was no change in the melt viscosity of the 40-mesh pine based composite, when the filler percentage changed from 40% to 60% (Figure 2.7). Identical formulations evaluated with the slit die showed a difference in melt viscosity with pine content. Using the slit die, the results from both the maple and pine indicate that an increase in the wood filler percentage produces an increase in the shear viscosity of the melt. The inconsistency with the previous capillary rheology may result from the differences in thermal histories and size effects. Pine species are known to produce substantial levels of natural stearates with chemistries similar to some lubricants. Increased soak times or extrusion temperatures may result in increase migration of the components to the particle surface. Li and Wolcott (2004) also indicated that at a 40% filler level, the shear flow curves of the pine-based melt were dependent on the die dimensions. Since there is a difference in the dimensions of the slit die and the capillary die, there may be differences in the shear viscosity results. However, both of these causes are purely speculative and require additional research.

A comparison of different mesh sizes and percentages was also made in relation to HDPE/maple composites. Note that similar trends developed for both the 40-mesh and 60-mesh filled composites. As seen in Figure 2.8, the results are much like those observed in the pine-based formulations where an increase in the wood filler increased the viscosity of the melt. Also, note that as the mesh size of the wood filler decreased, the viscosity decreased. When comparing the viscosity of the pine and maple composites, it appeared that the pine formulations produced a slightly lower viscosity as compared to maple (2.8).

2.6.4 Shear Stress

While the shear viscosity results are of great value to the die designer, the importance of correctly determining the changes in the shear stress cannot be overlooked. For flow between two parallel plates, the shear stress of the flow is zero at the center and increases linearly as it approaches the edges of the channel. Therefore, the location of the highest shear stress is at the wall edge. In the case of plug flow, the polymer is not shearing and acts like solid flowing through the channel. In other words, the shear stress in the melt is zero throughout the height of the channel (Thorsteinsen, 2003).

The shear stress for a variety of different maple and pine formulations is presented in Figures 2.9-2.12. Since other research outlining the changes in shear stress of the melt for WPC formulations have not been located, all of the comparisons were made to similarly filled polymeric systems. In calcium carbonate ($CaCO_3$) filled PP systems, it has been shown that when the percentage of $CaCO_3$ in the composition is increased, the shear stress of the melt also increases (Han, 1974). Similar results are seen in Figure 2.9 with the maple formulations. As the maple filler percentage increases from 30 to 70%, the shear stress of the melt increases throughout the entire shear rate spectrum. At both the 60% and 70% wood loadings, the shear stress values deviated slightly from what was expected. This deviation may be due to the problems encountered with the feeding of the material.

The change in shear stress between different particle sizes of maple is not as pronounced as the change in wood filler percentage (Figure 2.10). While at first glance it appears that there is a weak trend toward an increased shear stress with decreased mesh sizes, this conclusion cannot be made. The data for the 40-mesh size on average has the highest shear stress values, but the three other mesh sizes reveal little difference. Therefore, it would be premature to draw any conclusions that an increase in shear stress is seen as the mesh size decreases.

It is also important to examine any differences between the shear stress of maple and pine based melts. Both pine and maple, while having different interfacial interactions with the plastic (Li and Wolcott 2004), produce very similar shear stress trends. In Figures 2.9-2.12 differences in the shear stress of these pine and maple based WPCs are shown. In both species, shear stress increases with wood content. The 40-mesh maple formulations showed a 136% increase at lower shear rates, and a 142% increase at higher shear rates when the wood level increased from 40 to 60%. Similar results were obtained in the pine formulations when filler content changed from 40 to 60%. In this case, a 78% increase in shear stress was observed at lower shear rates and 80% increase was observed at the highest shear rate. Similarly, when the particle size was increased from 40 to 60-mesh in the pine formulation, the shear stress of the melt increased by a maximum of 98 percent. This would indicate that the biggest influence on shear stress is not the mesh size, but the wood filler percentage in the WPC.

2.6.5. Extruder Motor Current

Changes in the current draw indicate total energy required to compound and flow the composite melt in the extruder. Differences can easily be seen in Figure 2.13 from 30 to 70% of 40-mesh maple. Overall, the melt viscosity increased with increases in the percentage of wood flour. Some of the deviations within the motor current results may be attributed to the resolution of the display as it only displayed 1.0 amp changes. The increased current indicates increased viscosity during the combined blending and flow stages of the extrusion process. This conclusion was compared against the different mesh size viscosity results of Figure 2.6. As expected, the shear viscosity results also indicated an increase in viscosity with a decrease in mesh size along with the increases current draw (Figure 2.14).

2.7 Conclusion

While little research has been published in relation to the WPC rheology, the importance of understanding the melt flow properties is very important. Therefore, this research was two-fold. First, to prove that the designed slit die produced reasonable flow properties for WPCs and, secondly, to show that results were similar to findings in the literature. In examining the results obtained in this research, distinct changes where noticed in the shear viscosity of the melts when the formulation was run on a slit die versus capillary rheometer.

For most of the melts, the slit die produced results that were considerably lower than the capillary rheometer. However, as the wood content in the blend increased, the closer the results of the two rheometers were to one another. It is believed that this difference is due to morphological differences in the melt from the two different processing conditions of the rheometers. The second noticeable result is that, unlike previous capillary rheometry research, the slit die viscosity results showed that changes in wood filler percentage in pine-based composites affect the shear viscosity of the melt. This is different from previous work, which indicates that similar viscosities where obtained for the two dissimilar pine-based WPC formulations.

The shear stress results of this research appear to be in good agreement with other work when filler percentages are compared. As the filler percentage of the wood increased from 30% to 70% in the melt, it was determined that the melt shear stress also increased. However, when mesh size effects on shear stress were examined, little change in the shear stress was noticed. Similar trends were noticed in the required current draw of the motor, as an increase in the wood filler percentage caused an increase in the required amperage to turn the motor.

Since the slit die has been proven to be an accurate tool for characterizing the rheological properties of WPC melts, further work into a full analysis of the pine-based composites is needed to see if wood filler percentage has a similar affect on both the shear viscosity and shear stress. In a comparison of 40% and 60%, it appears that pine will follow similar results to those obtained by maple. However, it would also be of interest to see if similar changes in the shear stress and shear viscosity would be observed if the mesh size of the pine based composite was changed.

Since a variety of different polymers are used in the manufacturing of WPC, it is of great interest to see if similar characterizations of the rheological properties of these polymers can be achieved. Therefore, further work into the analysis of these polymers melts using this slit die rheometer will be attempted.

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2.9 Figures

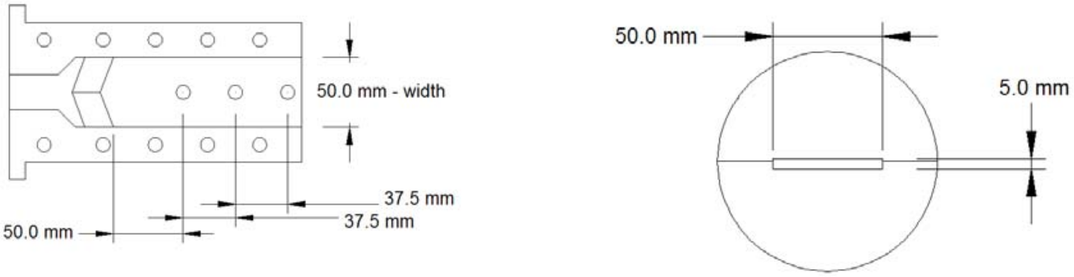

Figure 2.1. Top and end view of slit die schematic

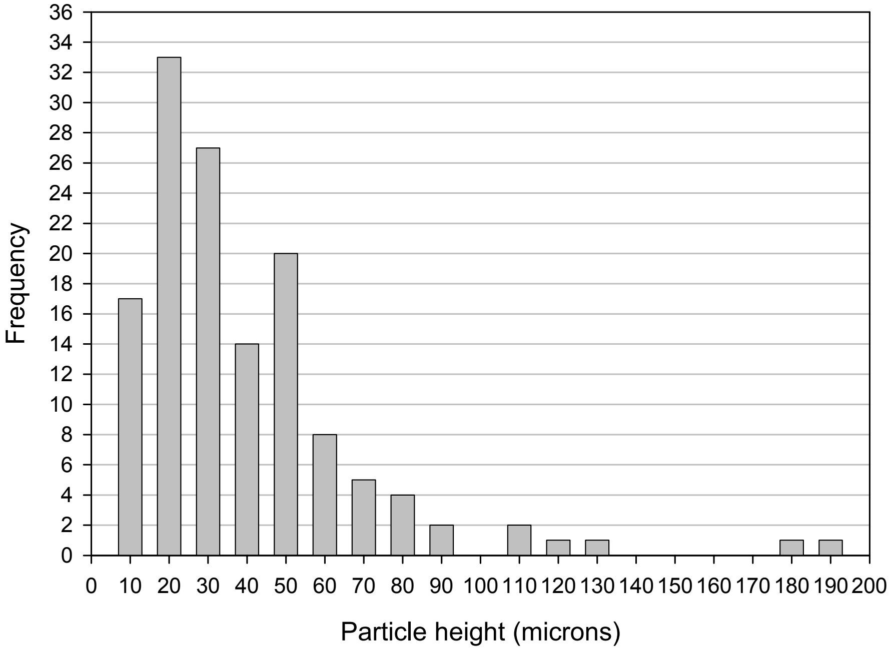

Figure 2.2. Particle height distribution

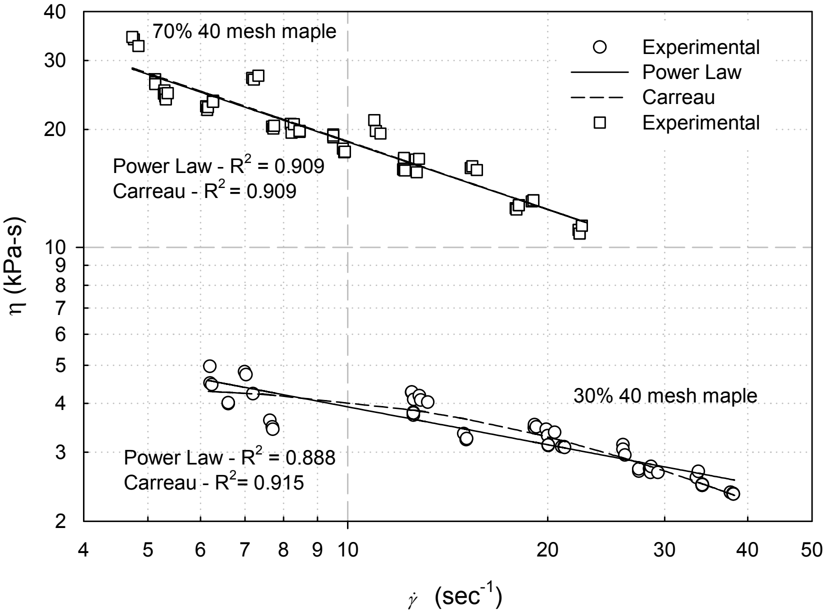

Figure 2.3. Carreau and power law curve fits for 30% 40-mesh maple and 70% 40-mesh maple formulations

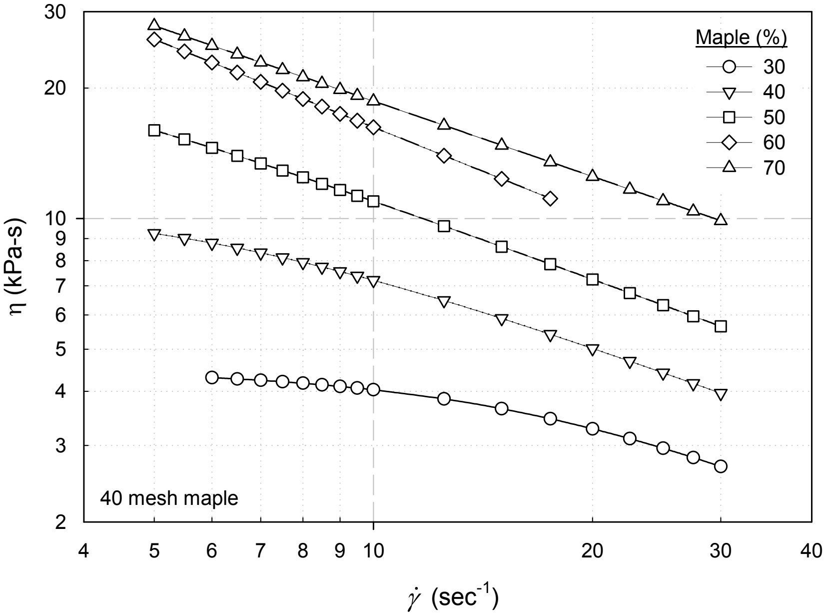

Figure. 2.4. Shear viscosity results for 30%-70% HDPE/wood composites

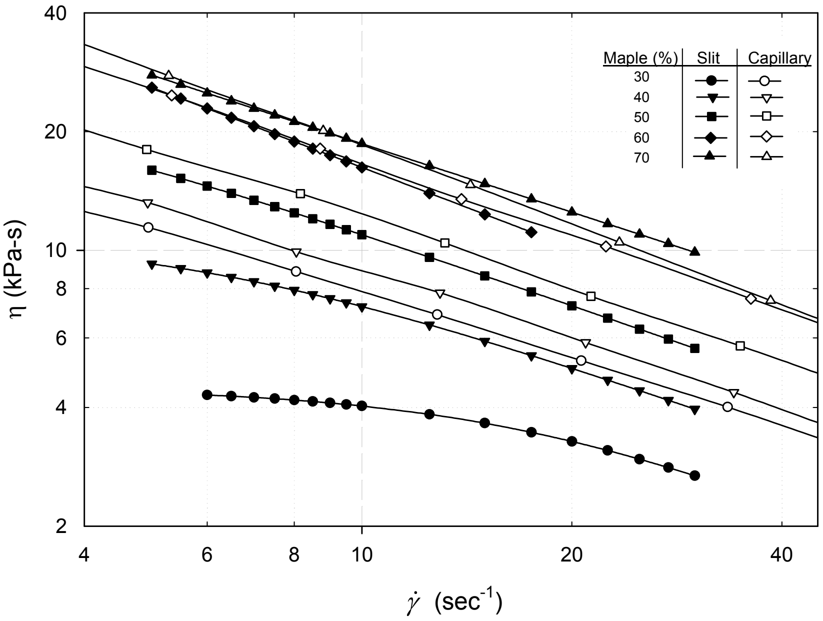

Figure. 2.5. Shear viscosity results for a 40-mesh maple based WPC

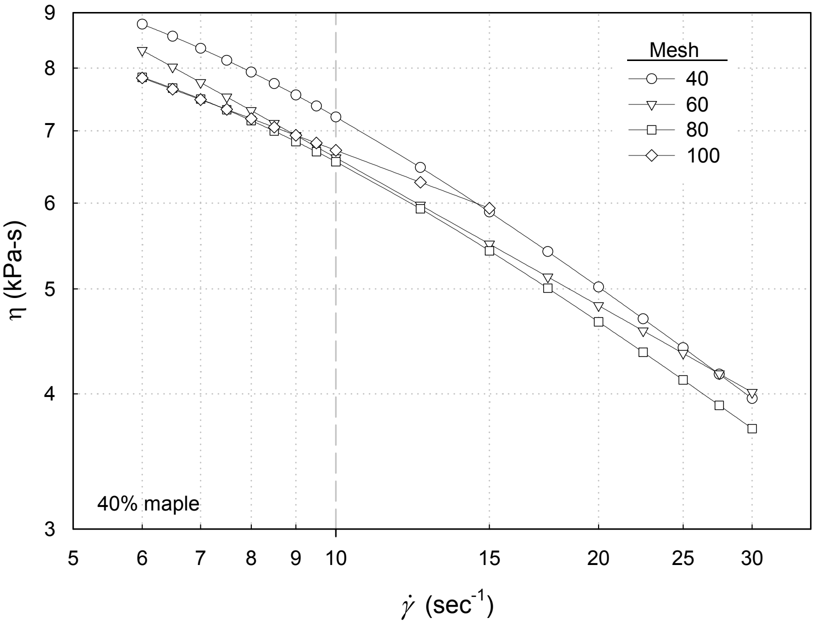

Figure. 2.6. Shear viscosity results for 40, 60, 80 and 100-mesh maple composites

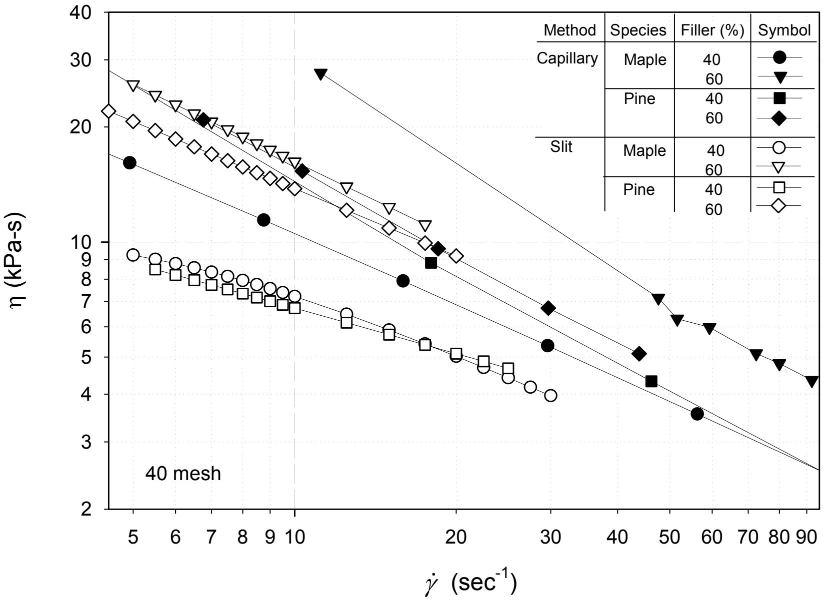

Figure. 2.7. Comparison of capillary die and slit die rheometry results

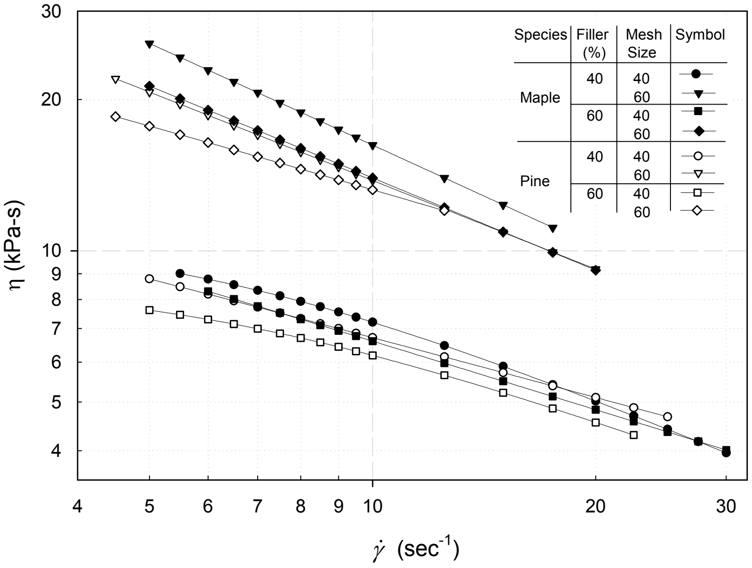

Figure. 2.8. Comparison of HDPE/wood composite blends viscosity results

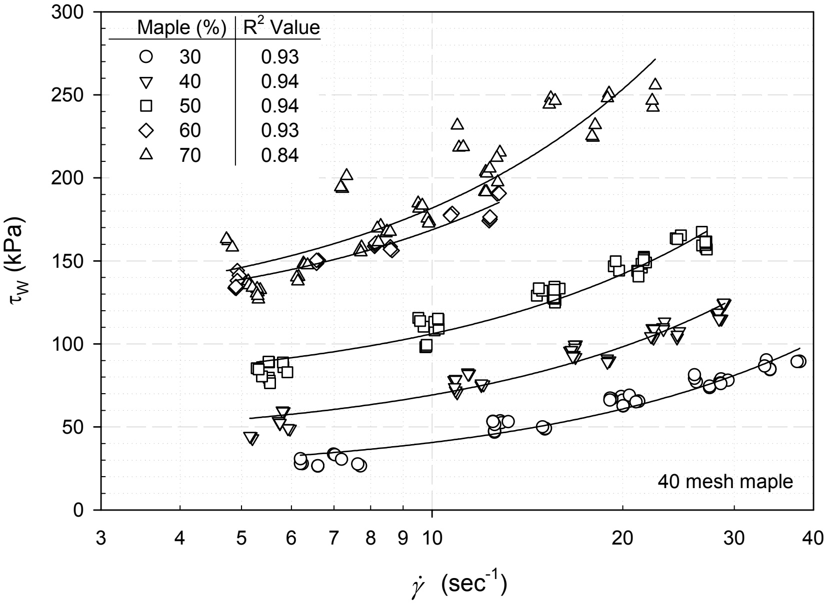

Figure 2.9. Shear stress of HDPE/wood composites

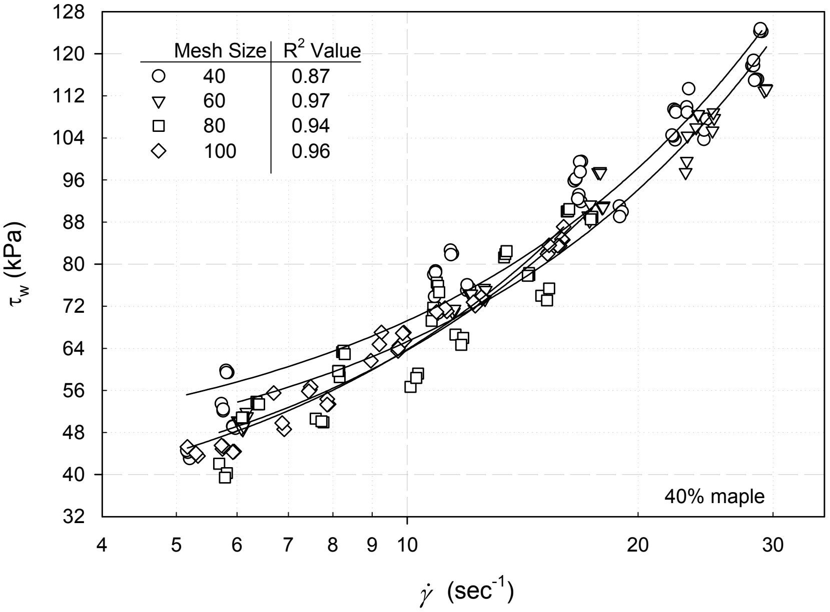

Figure 2.10. Shear stress of HDPE/maple composites with a variation in mesh size

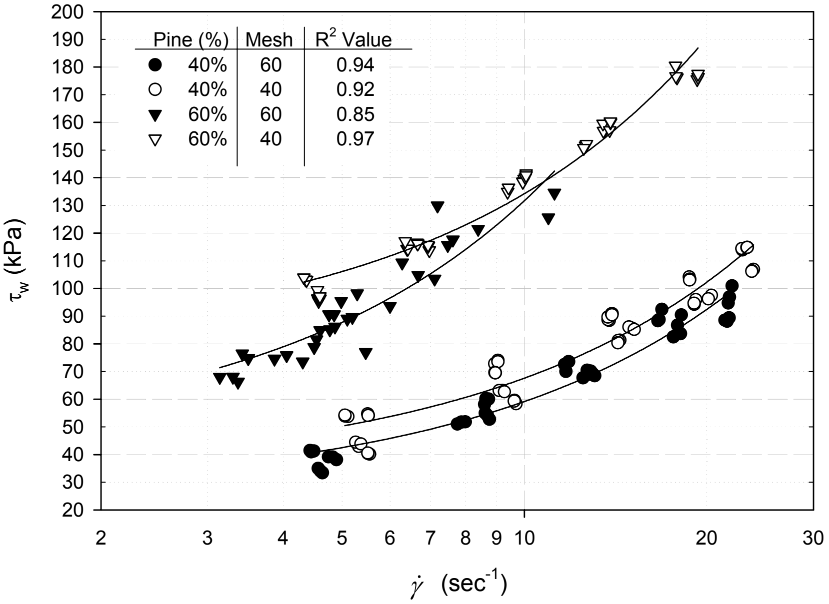

Figure 2.11. Shear stress of pine based wood plastic composites

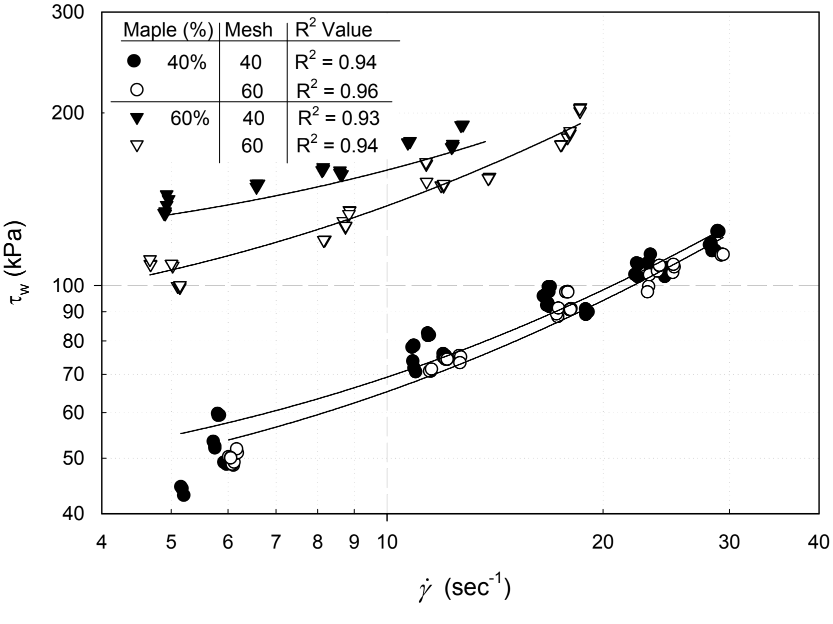

Figure 2.12. Shear stress of maple based wood plastic composites

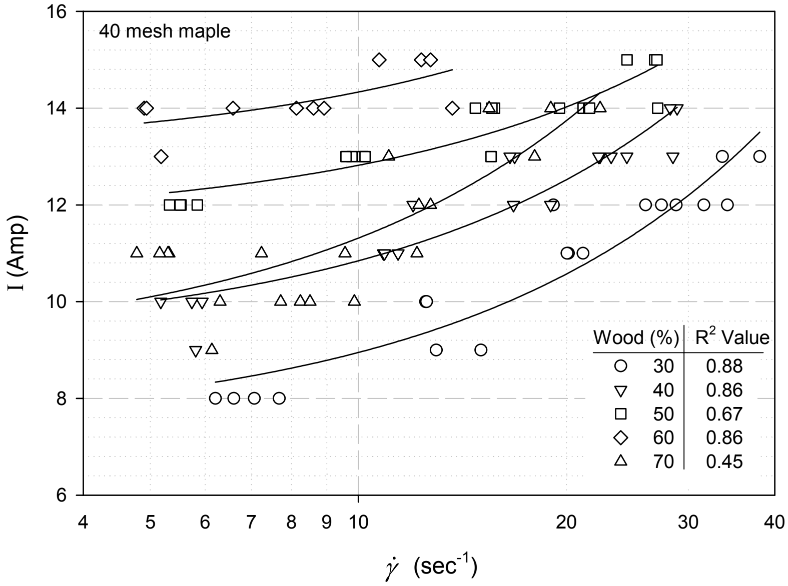

Figure 2.13. Changes in extruder motor current due to melt formulation changes. Linear regression curve fits shown for trend deciphering

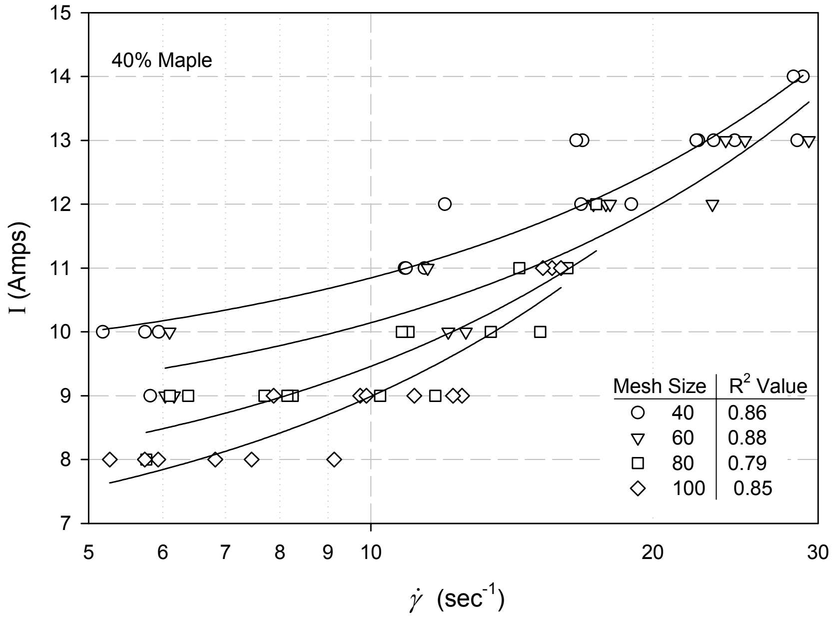

Figure 2.14. Effect of maple mesh size on the current draw of the extruder motor

2.10 Tables

Table 2.1. Material formulations

Formulations	n	η_0 (kPa-s)	λ
30(40M)70(PE)	0.254	4.48	0.057
40(40M)60(PE)	0.379	10.88	0.166
50(40M)50(PE)	0.381	25.96	0.390
60(40M)40(PE)	0.323	109.66	1.676
70(40M)30(PE)	0.422	167.01	4.452
40(60M)60(PE)	0.543	18.25	0.919
60(60M)40(PE)	0.389	83.31	1.854
40(40P)60(PE)	0.602	16.49	0.950
60(40P)40(PE)	0.413	94.28	2.642
40(60P)60(PE)	0.466	8.70	0.161
60(60P)40(PE)	0.567	34.02	0.879
40(80M)60(PE)	0.400	9.44	0.154
40(100M)60(PE)	0.695	14.38	1.206

Table 2.2. Carreau curve fit values

Table 2.3 Carreau-Yasuda Values

Formulations	n	η_0 (kPa-s)	λ
30(40M)70(PE)	0.254	4.48	0.057
40(40M)60(PE)	0.379	10.88	0.166
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CHAPTER 3 – RHEOLOGY OF ABS/WOOD COMPOSITES

3.1 Abstract

While the use of wood plastic composite (WPC) materials in a variety of residential building applications has continued to increase, the amount of rheological research on these materials has been has not. Most of the research into the rheology of these materials has been concentrated on the use of polyolefin-based resins as the matrix. However, the use of acrylonitrile-butadiene-styrene (ABS) resin is increasing, as producers are looking to exploit its excellent mechanical properties. Using a rheological slit die, the shear viscosity and shear stress of ABS filled with 40-mesh maple wood flour was studied. The results indicate that as the amount of wood filler or temperature of the melt increased, the viscosity of the melt decreased throughout the entire shear rate range investigated. From these viscosity results, a single master curve was developed that allows for theoretical viscosity values to be determined at higher shear rates. Applying an Arrhenius curve fit to the shifting factors, the activation energy of the 30%, 35%, and 40% filled melts was found to be 224.6, 298.0 and 286.5 kJ/mol. The shear viscosity of a high impact ABS was also tested and reduced through the addition of styrene-acrylonitrile (SAN) to the melt. The addition of the SAN polymer into the melt caused the viscosity of the melt to decrease. When these viscosity results were compared to HDPE based WPCs, the viscosity of the ABS melt was 228.7% higher. The shear stress results obtained using the slit die indicate identical trends as to those observed in the melt viscosity results.

3.2 Introduction

Research regarding wood filled thermoplastics did not begin to grow until the late 1980's. By combined efforts of the wood and plastics industries, wood plastic composites (WPC) were developed. As the research and commercial development of filled thermoplastics expanded, there has been an improved sophistication of the processing techniques, which in turn has led to an improved overall product performance (Wolcott and Englund, 1999). Today, this industry has grown into a major player within the residential building market, with WPC production reaching almost 700 million tons by the end of the 2001 (Clemons, 2002). As the increased demand for these products continues, manufacturers will continually be pushing new products to market. For these products to continually meet customer requirements, a variety of product development, manufacturing and mechanical testing needs to occur.

Most of the WPC research to date has concentrated on the mechanical properties of these materials (Sombatsompop and Phromchirasuk, 2004; Djidjelli et al., 2002). However, to capitalize on mechanical property developments in actual products, a better understanding of the processing flow conditions must be developed. Processing properties are especially important because manufacturing conditions and methods can have a strong influence on overall mechanical properties of the composite (Liang, 2002).

Most of the research on rheological behavior of wood-filled thermoplastics concentrates on the use of high-density polyethylene, polypropylene and polyvinyl chloride as the matrix material (Chastagner, 2005; Li and Wolcott, 2004, 2005; Sombatsompop, 2004, Shah and Matuana, 2004). Within the commercial WPC community, the use of amorphous styrenic resin composites is gaining interest in an effort to exploit the (1) excellent mechanical properties, (2) natural polar interactions with the wood fiber, (3) many options for weatherable cap stocks, and (4) paintability of these polymers. This group of styrenic resins includes polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), and styrene-acrylonitrile (SAN). Amongst the styrenic resins, ABS has been the most widely used, since it can lead to a stiffer foamed composite than the other resins (Schut, 2001).

In order to answer some of the unknown questions regarding the flow properties of ABS/wood composite melts, an on-line slit die rheometer will be used to determine the important rheological parameters. Using a technique developed by Chastagner (2005), the viscosity, shear rate and shear stress for a variety of ABS/wood composite blends will be quantified. This will allow for an investigation into the influence of different ABS resins, percentages of wood flour and temperature on these melt behavior parameters.

3.3. Literature Review

The manufacturing process for ABS resin begins with particles of crosslinked rubber being grafted into an elastomer phase and subsequently embedded into a continuous resin matrix (Casale et al., 1975). This crosslinked rubber phase provides ABS with many excellent properties including impact, toughness, hardness, and bondability. These properties facilitate the extensive use of ABS in the automotive and consumer electronics industries (Boldizar and Moller, 2003).

While research into the mechanical properties of ABS-based materials is prevalent, the amount research on ABS rheology is more limited. In the absence of rheological studies on wood filled ABS materials, inorganic fillers such as $CaCO_3$ (Liang, 2002; Tang and Liang, 2003; Liang, 2004), glass beads (Yilmazer, 1989), glass fibers (Ozkoc et al., 2004) and mica (Pastorini and Nunes, 1999) will be reviewed. The additions of these fillers to the melt, alters the rheological properties in dramatic ways. First, the viscosity of the melt tends to increase with filler content. When Liang (2002, 2004) and Tang and Liang (2003) added $CaCO_3$ to virgin ABS polymer, the melt viscosity of the composite increased dramatically with a corresponding increase in $CaCO_3$ percentage. Nano-$CaCO_3$ particles produced little change in the viscosity below 20% filler level, where upon higher filler levels increased the viscosity of the melt at least three fold. Liang also found that these increases in viscosity were independent of testing temperature.

When glass beads and fibers were used as a filler (Yilmazer, 1989), similar increases in the viscosity were noted. Glass beads generally change melt viscosity throughout the entire shear rate range analyzed. However, this was not the case for glass bead filled ABS, where an increase in the viscosity was only noted at low shear rates. As shear rate increased, the viscosity converged, with no dependence on filler percentage. Similar results were obtained when glass fiber was used as filler, however, the increases in viscosity were less pronounced than with the glass bead filler.

Within the WPC literature, the rheology of wood-filled polyolefins has also been examined. Li and Wolcott (2004) have researched the changes in the rheological properties of both pine and maple based HDPE composites using a capillary rheometer. This work indicated that like inorganic filled ABS, increased filler content resulted in similar increases in melt viscosity. This is due to the increased amount of wood flour particles within the melt inhibiting the overall flow of the material as it moves through the die, thus causing the increased shear viscosity. Li and Wolcott observed little change in the melt viscosity due to different wood mesh sizes used. These capillary results were expanded on by Chastagner (2005), who used an on-line slit die to test similar HDPE filled formulations. The shear viscosity results obtained using the slit die allowed for similar conclusions with respect to particle size effect and wood filler content. The influence of wood species was examined and it was determined that both the maple and pine filled melts produced similar viscosity results. Chastagner also examined the affects of different wood filler content and mesh size on the shear stress. There was indication that increasing wood content increased the shear stress for both maple and pine based melts. This result was similar to finding $CaCO_3$ filled PP (Han, 1972). However, mesh size resulted in little effect on the shear stress.

3.4 Materials

The rheological experiments were performed using both acrylonitrile-butadiene-styrene (BASF GP-22, MFI = 17.7 cm^3/10min) and a blend of ABS (BASF HI-10, MFI = 8.0 cm^3/10min) and SAN (BASF LURAN 358N, 22 cm^3/10min). These polymers were then filled with different percentages of 40-mesh maple wood flour (*Acer spp.*) (American Wood Fiber, 04010). The amount of wood flour varied from 20 to 40-wt%. A full listing of these material formulations is found in Table 3.1. The wood flour was dried from 8 to < 3% moisture content in a steam tube dryer (Louisville Dryer Company) operated between 153-164° C (307-327° F). The polymers were used in pellet form as received. All composite formulations were dry blended in 1.2 m. drum tumbler for 10 minutes to facilitate an initial mixing of the polymer resins and wood flour.

3.5 Methods

3.5.1 Slit die measurements

A slit die rheometer with a height of 5.0-mm and a width of 50.0-mm was attached to a 35.0-mm twin-screw extruder (Cincinnati Milicron CM-35). A thorough description of both the design and verification of the slit die rheometer is presented elsewhere (Chastagner, 2005).

The rheological values are calculated from the slit die using equations developed by Han (1971, 1974), Eswaran (1963) and Wales (1965). To accurately determine the pressure gradient along the longitudinal length axis ($-\partial p / \partial x$) of a slit die, a minimum of three pressure transducers is required. The shear stress and shear viscosity can easily be calculated. The derivation of the slit die equations is rather complicated and is presented by Han (1974), however, a brief description of the pertinent equations will be given here. With the determination of shear stress at the die wall (τ_w):

$$\tau_w = \left(\frac{\partial p}{\partial x} \right) \frac{h}{2} \tag{1}$$

where *h* is given as the slit height. The apparent shear rate ($\dot{\gamma}_a$) is defined by:

$$\dot{\gamma}_a = \frac{6Q}{wh^2} \tag{2}$$

where w is the width of the slit die, and Q is the volumetric flow rate. The true shear rate ($\dot{\gamma}$) can thus be determined using a Rabinowitsch correction:

$$\dot{\gamma} = \left(\frac{2n+1}{3n} \right) \dot{\gamma}_a \tag{3}$$

where n is the Rabinowitsch correction factor. The true shear rate with the substitution of the Rabinowitsch correction is rewritten as:

$$\dot{\gamma} = \left(\frac{2}{3} + \frac{1}{3} \frac{d \ln \dot{\gamma}_a}{d \ln \tau_w} \right) \dot{\gamma}_a \tag{4}$$

3.5.2 Carreau-Yasuda curve fitting

To predict the viscosity of the melt over a wide range of shear rates, a five parameter Carreau-Yasuda (Carreau, 1996) (C-Y) model was applied to each formulation:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} \approx \frac{\eta}{\eta_0} \approx \frac{1}{\left[1 + \left(\lambda \dot{\gamma} \right)^a \right]^{\frac{1-n}{a}}} \tag{5}$$

where a, n, λ, are all curve fitting parameters, and η_∞ and η_0 are the viscosity of the melt at infinite and zero shear, respectively. Initial calculations of the applied C-Y curve fits showed that “a” had a value near 12 for a vast majority of the formulations. Therefore, “a” was constrained to be 12 for the all of the C-Y curve fits. The curve fitting parameters and η_∞ where determined by using a generalized reduced gradient algorithm (Microsoft, 2005) over 1000 iterations.

The vast majority of the data presented in the shear viscosity results appears to be linear when plotted on a bi-logarithmic plot. However, if the entire shear rate range were analyzed, it is expected that the data would not be linear. In most polymeric systems, a plateau is achieved at lower shear rates and then the viscosity curves downward into a linear region as the shear rate is increased. Therefore, a power law regression could only be applied accurately to the linear appearing region. All of the viscosity curves presented in this paper are presented using the C-Y curve fit to avoid unnecessarily clutter. A representative fit of the C-Y curve to the experimental data is shown in Figure 3.1.

3.5.3 Time-Temperature Superposition

The rheology of polymer melts is sensitive to changes in temperature. The theory of time-temperature superposition allows one to relate changes in viscosity and relaxation time to changes in temperature (Bird et al 1987). By determining the rheological properties of the melt at a variety of temperatures, a single master curve at a specific temperature can be developed to predict the viscosity of the melt over broad range of shear rates. The development of the master curve is given by Collier et. al (2003) and is accomplished by determining a shift factor (a_T) for the zero shear viscosity results:

$$a_T = \frac{\eta_0(T)T_{ref}\rho_{ref}}{\eta_0(T_{ref})T\rho} \tag{6}$$

where T_{ref} is the reference temperature, T is the prevailing temperature, ρ_{ref} and ρ are the density values of the melt at the reference temperature and prevailing temperature, $\eta_0(T)$ and $\eta_0(T_{ref})$ are the zero shear viscosity at the prevailing and reference temperature, respectively. For polymeric melts it is assumed that $(\rho_{ref}T_{ref})/(\rho T)$ is equal to unity (Helleloid, 200; Bird et al., 1987). The zero shear viscosity can be determined through the use of the C-Y curve fit, however the results from this research do not cover a sufficient range of shear rates to confidently develop predictions for $\eta_0(T)$. The reduced shear rate ($\dot{\gamma}_r$) can be determined by:

$$\dot{\gamma}_r = a_T\dot{\gamma} \tag{7}$$

with the reduced viscosity (η_r) determined through:

$$\eta_r = \frac{\eta(T,\dot{\gamma})}{a_T} \tag{8}$$

where $\eta(\dot{\gamma},T)$ is the viscosity at the prevailing temperature and shear rate. By graphically aligning the different temperature curves in a plot of η_r vs. $\dot{\gamma}_r$, the required shifting factors for each of the melt temperatures can be determined through the simultaneous use of equations (7) and (8). The required shifting factors are then related to temperature through the use of an Arrhenius equation (Miller and Rothstein, 2004):

$$a_T = \exp\left[\frac{\Delta H}{\bar{R}}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{9}$$

where $\bar{R}$ is the universal gas constant and ΔH is the activation energy of the melt.

3.5.4 Experimental Techniques

Using a sampling technique described elsewhere (Chastagner 2005), the rheological values for a variety of melts were obtained. Five different temperature profiles of 180, 185, 190, 195 and 200° C. were used for the GP-22 analysis, while the HI-10/SAN blends were evaluated at only 190° C. The prevailing test temperature was used for all extruder and die zones. Filled ABS melts are more typically evaluated at temperatures above 220° C (Yilmazer, 1989), which are higher than those tolerable by the thermally sensitive wood particles. It should also be noted that while previous work by Chastagner (2005) on the identical slit die included higher shear rates, the shear rate range for this set of experiments was limited to a lower shear rate range, because of the higher melt viscosities and the limits imposed by the extruder motor.

3.6 Results

3.6.1 Shear viscosity results

The influence of wood filler level, SAN polymer and temperature on the shear viscosity of ABS filled melts was examined using a slit die. In general, the shear viscosity of the melts increased with an increase in wood filler level. Similar increases in melt viscosity were seen with decreasing temperature and SAN filler content.

The influence of SAN content on the viscosity of a high impact ABS grade (HI-10) filled with 30% maple flour was evaluated at 190° C (Figure 3.2). In these formulations, the SAN content was varied from 0 to 20% of the total polymer content in the formulation. Using a C-Y curve fit for each of the formulations (Table 3.2), the melt viscosity of these formulations were found to decrease with increasing SAN content. The shear viscosity of the HI-10 filled with 25%SAN was compared to a similar GP-22 formulation, the viscosity of the SAN filled melt was up to 24.6% higher than the comparable GP-22 melt (Figure 3.2). When the shear viscosity of the 20% SAN filled melt was compared to a 30% HDPE-70% maple melt (Chastagner, 2005), the SAN shear viscosity was up to 228.7% higher than the HDPE viscosity despite the fact that it was evaluated at 180 rather than 190° C.

Since the influence of SAN into the ABS/wood melt affected the shear viscosity, it is important to examine the change in melt viscosity due to changes in the wood filler amount and temperature. When the shear viscosity of GP-22 filled with 30% maple was tested, there was a distinct decrease in the melt viscosity as the temperature of the melt decreased (Figure 3.4). When the effects of temperature were tested on maple filler percentage of 35 and 40% (Figure 3.5), identical results were observed. This increase in viscosity is expected because, as the temperature decreases, there is a reduction in the amount of chain movement within the polymer, leading to more resistance within the melt to deform.

However, if the temperature of the melt was held constant and instead the maple flour content was varied, from 20 to 40%, the shear viscosity was found to increase with increasing wood levels (Figure 3.3). Similar increases in shear viscosity have also been found with HDPE/wood melts tested a slit die rheometer (Chastagner, 2005) and a capillary die rheometer (Li and Wolcott, 2004).

3.6.2 Viscosity Temperature Dependence

Since the shear viscosity of the GP-22 filled with 30, 35 and 40% maple flour was found to decrease as the temperature of the melt increased, these viscosity changes are then used for the construction of master curves. These master curves were developed by plotting the log (η_r) vs. log ($\dot{\gamma}_r$) for a given formulations C-Y curve fit at each specified temperature. The shifting of the fits was accomplished by graphically aligning the different temperature curves, to create a single, continuous master curve using 195° C as the reference temperature (T_{ref}). The master curve for 30% maple and 70% GP-22 at T_{ref} = 180° C is shown in Figure 3.4, along with the original C-Y curve fits (Table 3.3) and the resulting shift factors. The agreement of the data throughout the entire temperature range is good, allowing a single, consistent master curve to be developed. The shift factors decrease with increasing temperature and are well described using the Arrhenius equation as shown in Figure 3.6.

The master curves developed for 35 and 40% maple filler amounts display similar form, with increasing wood content resulting in increased viscosity (Figure 3.5). The respective shift factors are presented in Figure 3.6, along with the resulting Arrhenius parameters, including activation energy. Calculation of the activation energy allows for the determination of the minimum amount of energy input required by the system for chain segments of polymer to move from their present location to a new location (Rosen, 1993). Since there is a significant amount of energy required for the polymer chains to translate. Adalja et al. (2001) has shown that the addition of glass fibers dramatically increases the flow activation energy of low-density polyethylene. When the glass filler amount increased from 10 to 50%, the corresponding activation energy increased from 27.1 kJ/mol to 209kJ/mol, since the increase in the filler amount restricted the movement of the polymer chains within the melt.

The temperature of the melt when conducting the rheological test can also alter the required activation energy of the melt. At temperatures near the glass transition temperature (T_g), thermal influences on the melt are different than at higher temperatures. Near T_g (T_g< T< T_g+100º C.) the influence of temperature on ability of the polymer chain to move is dependent on its neighboring chains and therefore can be described using a WLF relationship (Ferry, 1980). However, at temperatures above approximately T_g+100º C. there is less interaction between the chains and the physical behavior of the melt changes. Therefore an Arrhenius fit is more applicable at these elevated temperatures (Kao and Bhattacharya, 1998).

When the flow activation energy of the GP-22 filled melts was calculated in this study using the slope of the of the shifting factors, the activation energy of the 30, 35 and

40% maple filled melts was determined using the Arrhenius fit to be 224.6, 298.0 and 286.5 kJ/mol, respectively. These activation energy values are higher than results obtained for unfilled ABS tested on a capillary die, with Casale et al. (1975) finding unfilled ABS activation energy values between 77.0 and 128.1 kJ/mol. This difference in activation energy may be attributed to two factors. First, the additional amounts of wood filler in the melt is likely to cause an increase in the activation energy, since composite melts have been found to be more temperature sensitive (Dweiri and Azhari, 2004). Secondly, as the temperature of the melt decreases, the polymer chains in the melt exhibit less interaction with their neighboring chains causing a reduction in their mobility. The relatively low temperatures necessitated by the thermally sensitive wood fibers are likely to decrease mobility causing an increase in the activation energy. The combination of these factors is only amplified by the addition of the filler restricting the flow of the melt (Chen et al, 2003).

3.6.3 Shear Stress Analysis

Since the determination of the shear viscosity is based on the calculated shear stress value, it is important to observe how the shear stress changes with the different formulations. Shear stress can also be used to quantify determine the slip velocity of the melt and if used in conjunction with a varying slit die height, the yield stress of the melt can be determined. Shear stress at the wall (τ_w) was determined for both the GP-22 and HI-10/SAN filled melts. As maple content of the GP-22 composite increased, the shear stress of the melt increased as well (Figure 3.7). Identical results were observed in the shear stress results of HDPE melts filled with maple wood flour (Chastagner, 2005). In addition, when filler content was held constant shear stress was an observed to increase with shear stress and decreasing temperature. This result was observed for the 30, 35 and 40% filler contents and a representative plot is shown in Figures 3.8. In general, the observed increases in shear stress result from higher resistant to flow and correspond with increased viscosity.

When the HI-10/SAN filled formulations were evaluated, shear stress results similar to the GP-22 melts were achieved. Although a general trend of decreased shear stress with increasing SAN content was noted, certain discrepancies exist and likely originate from the variability (Figure 3.9) of the results. As in the previous results, decreased shear stresses corresponded with viscosity reductions. For instance, the pure HI-10 formulation contains the highest rubber content and resulted in the highest shear stress values. Addition of SAN reduced the rubber proportion within the melt, reducing the resistance to flow and the required shear stress to move the melt.

3.7 Conclusions

While most of the focus of the WPC research and development has been centered on the use of HDPE and PP as a polymer matrix, the introduction of ABS as a viable replacement to these polymers, would allow for manufactures to apply the excellent mechanical properties of this polymer to an industry that is continually looking to expand its applications. However, to date, most wood filled ABS melt research has concentrated on the mechanical properties of the composite, with little work on the rheology of these systems.

The rheological research conducted in this study indicates that these ABS/wood systems act very much like other polymer systems filled with both wood and other inorganic fillers. Shear viscosity results indicate that as the temperature of the melts is increased, there is also an accompanying decrease in the shear viscosity. The changes in the melt viscosity due to temperature allowed for single master curves to be developed for the prediction of the shear viscosity at a wider variety of shear rates than can be tested. The activation energies of the 30%, 35% and 40% maple filled GP-22 melts were 224.6, 298.0 and 286.5 kJ/mol, respectively. Within the ABS based WPCs, there is also an indication that as the as the wood filler percentages within the composite increases, so does the viscosity of the melt. This result has also been seen in other work done on both ABS and HDPE filled melts.

The shear stress of the GP-22 based melt was found to be directly dependent on the amount of wood filler and temperature of the melt. Increases in shear stress were seen as the temperature decreased and the filler level increased. Both the GP-22 and HI-10/SAN formulations showed good overall agreement of the data from run to run, with the HI-10 results generally showing a decrease in the shear stress as the amount of rubber within the melt was lowered.

The results of this rheological study into wood filled ABS melts demonstrated that reasonable rheological results can be obtained for these types of materials and that the overall trends agree with previous work done by other authors. There is still more work that needs to be accomplished in regards to fully understanding the rheological changes in ABS/wood melts. However, this research provides an initial starting point for other work to be developed from, since the interaction of modifiers, lubricants and other additives on the rheological properties of the ABS/wood melts hasn’t even been addressed in this research.

3.8 References

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3.9 Figures

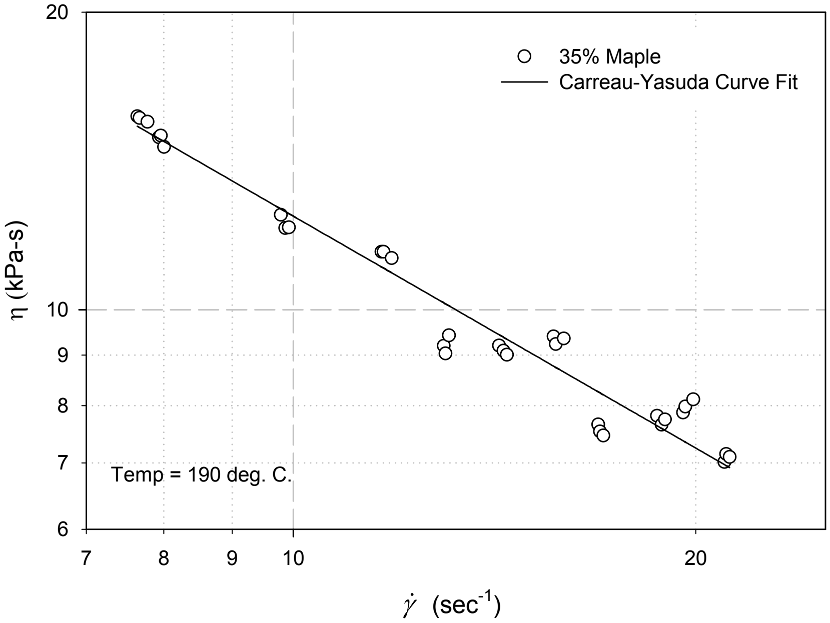

Figure 3.1 Representative Carreau-Yasuda curve fit of experimental data

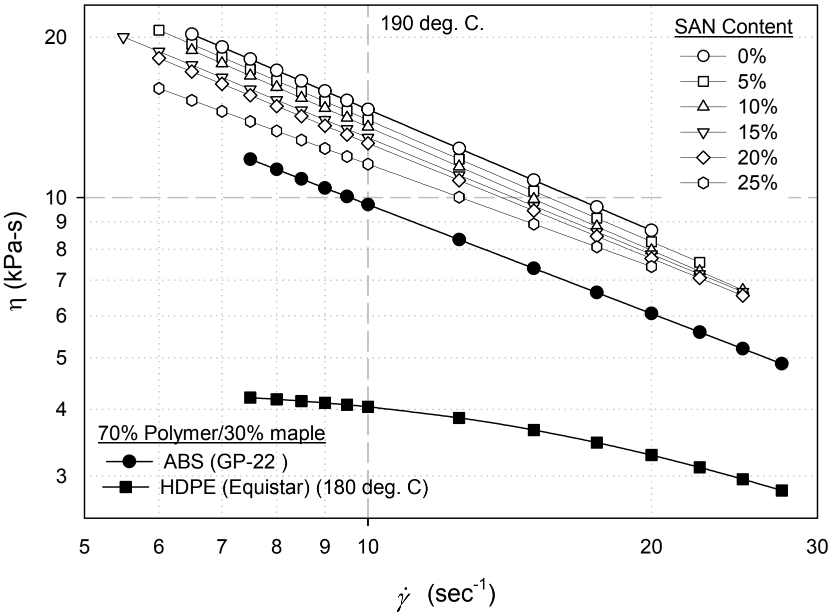

Figure 3.2. Shear flow curve of HI-10/SAN filled with 30% maple, with a comparison to GP-22 and HDPE filled melts

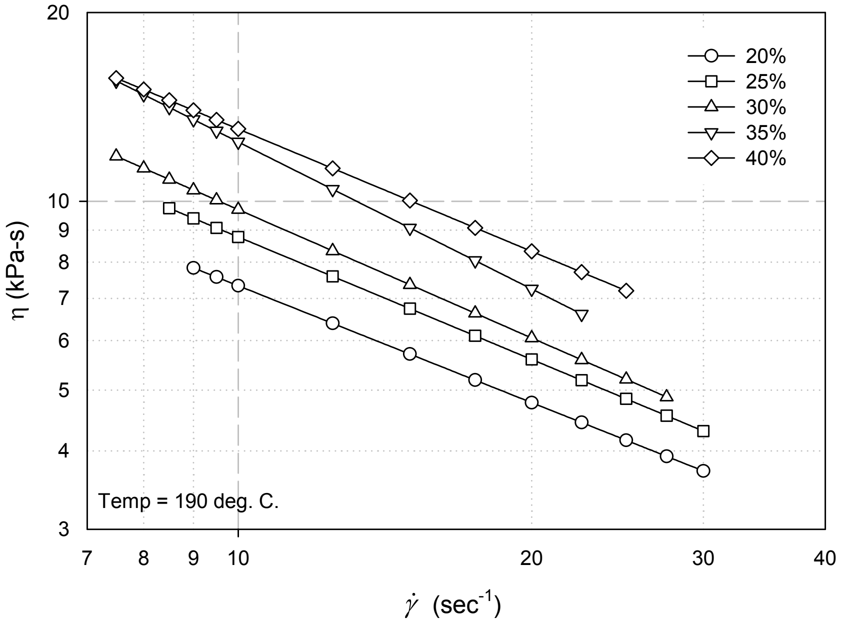

Figure 3.3. Shear flow curve of GP-22 filled with varying amounts of maple at 190°C.

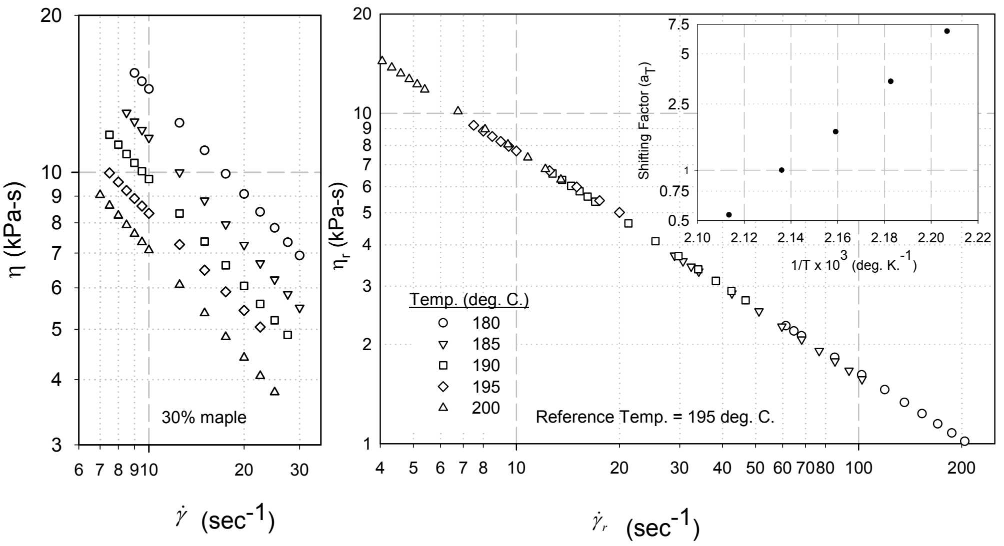

Figure 3.4. Un-shifted results shown with a developed master curve for GP-22 filled with 30% maple. Required shifting factors are also shown.

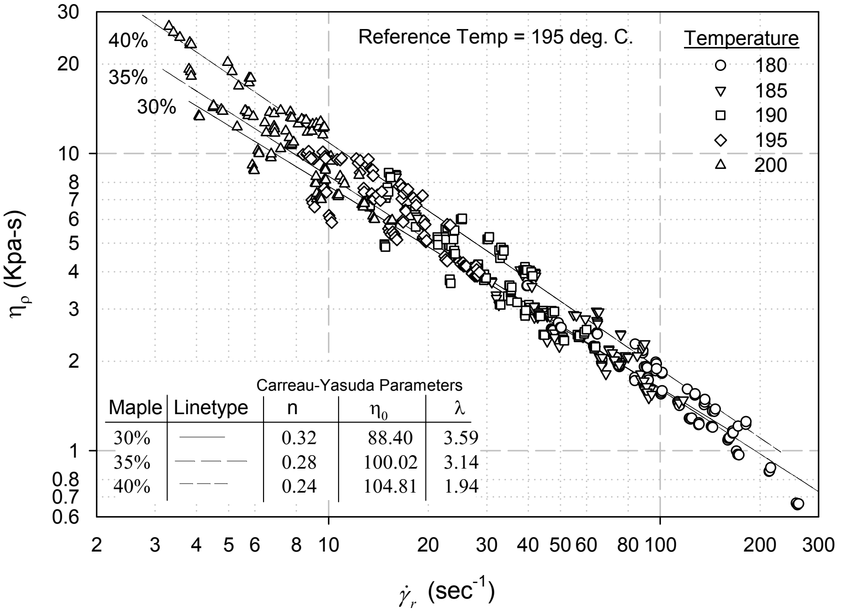

Figure 3.5. Master curve for 30, 35 and 40% maple filled composites, with regression lines indicating Carreau-Yasuda curve fits for actual shifted data.

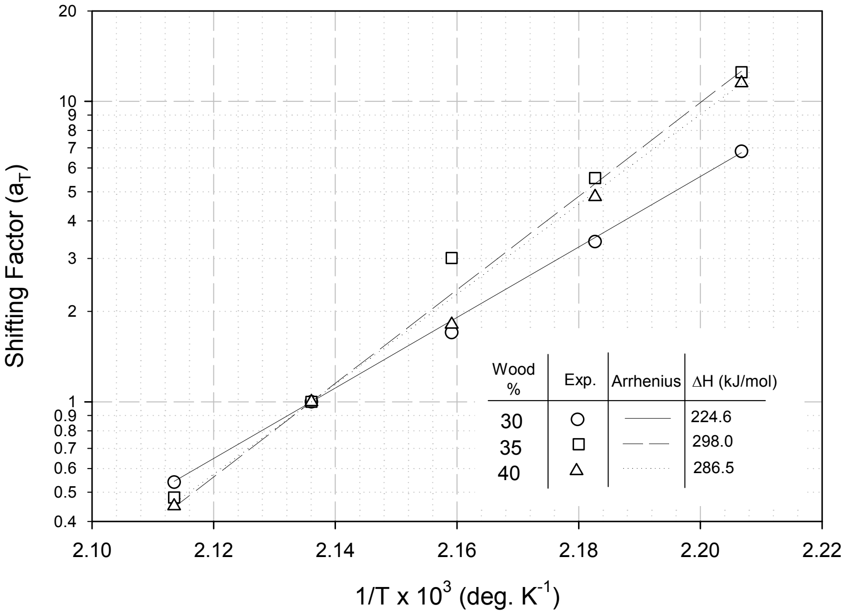

Figure 3.6. Actual shift factors shown with Arrhenius curve fits and required activation energy.

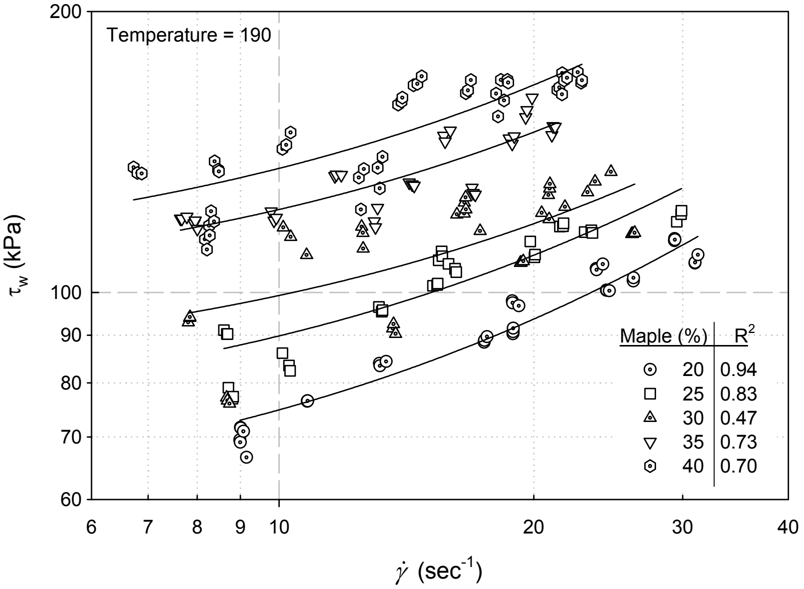

Figure 3.7. Shear stress of GP-22 filled with maple at 190°C. Linear regression curve fit also plotted to allow for determination of trends.

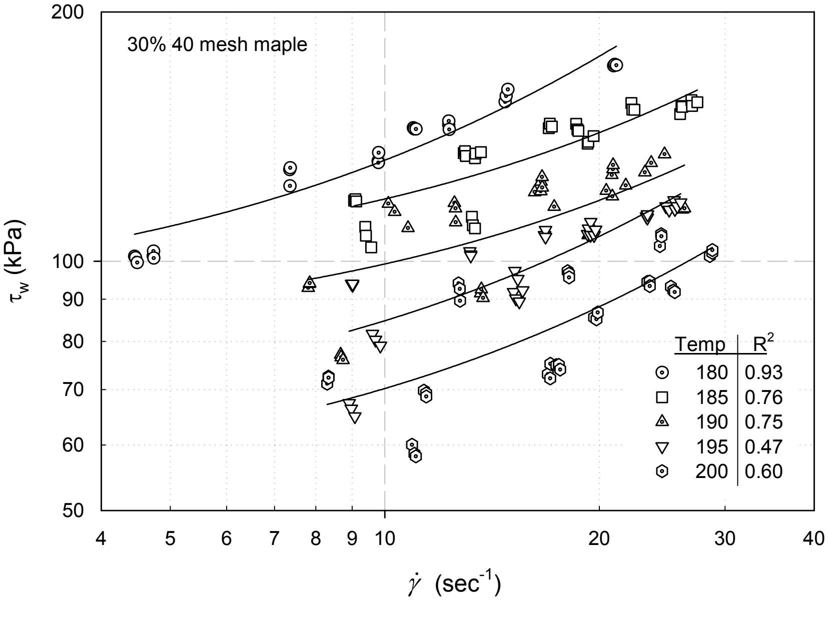

Figure 3.8. Shear stress of GP-22 filled with 30% maple at varying temperature. Linear regression curve fit also shown to facilitate trend determination.

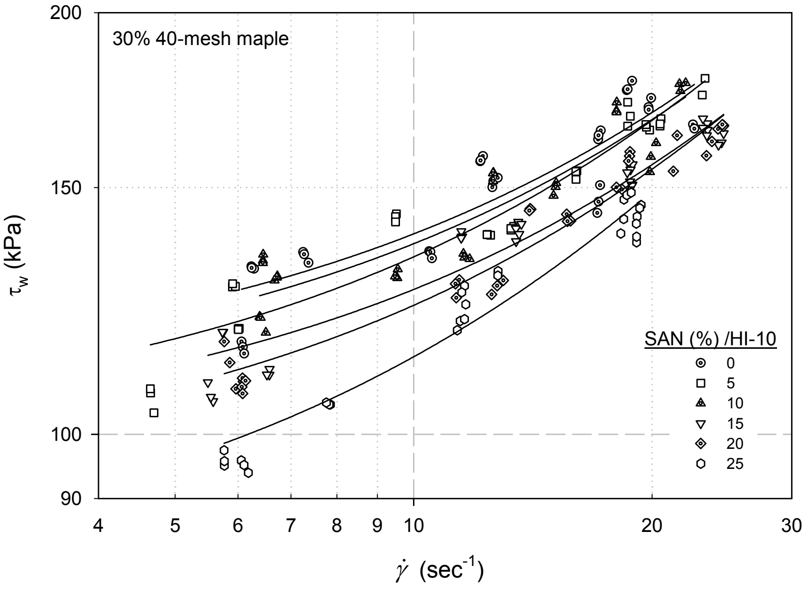

Figure 3.9. Shear stress of HI-10/SAN filled with 30% maple. Linear regression curve fit also plotted to allow for determination of trends.

3.10 Tables

Table 3.1. Material formulations for GP-22 filled with maple wood flour

Temp (°C)	Wood (%)	Plastic (%)
170	30	70
170	35	65
170	40	60
180	30	70
180	35	65
180	40	60
190	20	80
190	25	75
190	30	70
190	35	65
190	40	60
200	30	70
200	35	65
200	40	60
210	30	70
210	35	65
210	40	60

Table 3.2. Carreau-Yasuda values for GP-22 filled with maple

Temp (°C)	Maple (%)	n	η_0 (kPa-s)	λ
180	30	0.33	41.73	0.49
180	35	0.19	32.26	0.23
180	40	0.32	59.85	0.53
185	30	0.32	35.00	0.50
185	35	0.29	35.77	0.40
185	40	0.24	65.93	0.61
190	20	0.38	28.45	0.89
190	25	0.35	32.73	0.76
190	30	0.32	35.00	0.50
190	35	0.22	36.70	0.40
190	40	0.35	32.74	0.41
195	30	0.38	30.28	0.80
195	35	0.29	34.65	0.66
195	40	0.28	32.79	0.43
200	30	0.32	30.83	0.86
200	35	0.31	24.08	0.53
200	40	0.19	34.00	0.45

Table 3.3 Carreau-Yasuda values for SAN let down procedure

SAN	ABS (HI-10)	n	η_0 (kPa-s)	λ
0	100	0.25	34.39	0.31
5	95	0.24	33.95	0.32
10	90	0.23	33.75	0.33
15	85	0.27	32.78	0.36
20	80	0.28	31.71	0.36
25	75	0.36	29.94	0.44

CHAPTER 4 – CONLUSIONS AND FUTURE WORK

4.1 Conclusions

The market for wood plastic composites (WPC) continues to grow as their applications and subsequent use in residential building construction has increased. In order for manufacturers to keep cost low, accurate developmental testing of these materials is needed. To date, most of this research has centered on the mechanical properties of the final product, while little research has examined the flow behavior of the WPC melt while it is being extruded. Therefore, the intent of this research was two-fold. First, to prove that the designed slit die produced reasonable flow properties for WPC melts by comparing the results to capillary die results and secondly, to use the slit die to further quantify the rheological properties of HDPE and ABS filled with wood filler as a variety of variables were altered.

When the HDPE rheological results of the slit die were compared to results obtained using a capillary die, the slit die produced results that were considerably lower than the capillary rheometer. However, as the wood content in the blend increased, the closer the results of the two rheometers became to one another. It is believed that this difference in viscosity is partly influenced by the different processing conditions the melt undergoes in the two rheometers. A second noticeable difference between the results of the two methods is that unlike previous capillary rheometry research, the slit die viscosity results showed that changes in the wood filler percentage in pine-based composites can effect the shear viscosity of the melt. This is different from previous capillary results, which indicated that similar viscosities should be obtained for the two dissimilar pine-based WPC formulations. It is speculated that these observed differences in the slit die results might be caused by the pine wood filler producing natural lubricant like substances.

The slit die shear stress results for HDPE based melts appear to be in good agreement with results from other filled polymer systems. When the filler percentage of the wood was increased from 30% to 70%, the melt shear stress corresponding increased. However, when mesh size was altered, little change in the shear stress was noticed. Similar results were also observed in the required current draw of the extruder motor. As the amount of wood filler within in the melt increased, so did the required amperage to turn the motor.

Most WPC research and development is concentrated on the use of HDPE and PP as a polymer matrix. Recently, however, the use of ABS has become more popular as has become as manufactures look to apply its excellent mechanical properties to WPC products. Very little research on ABS based WPCs is known to exist within the open literature and relevant melt rheology literature for these composites is non-existent.

The rheological research conducted in this study indicates that ABS/wood composites behave similar to other filled polymer systems. Shear viscosity results indicate that as the temperature of the melt is increased, there is also an accompanying decrease in the shear viscosity. This observed change in melt viscosity is then used to develop master curves that aid in the determination of predicted shear viscosity results at shear rates that cannot be tested. By shifting the viscosity and shear rate using a calculated shift factors, the master curves showed an increase in the shear viscosity as the wood filler percentage within the ABS melt increased. Using the shifting factors and applying an Arrhenius fit to the results; the activation energy of the melts was calculated.

The activation energies of the 30%, 35% and 40% maple filled GP-22 melts were 224.6, 298.0 and 286.5 kJ/mol, respectively. These results were found to be higher than unfilled ABS flow activation energy values calculated from previous capillary die work. It is very possible that these differences are due to the added wood filler restricting the amount of possible motion within the polymer chains, thereby increasing the activation energy.

Comparisons of the GP-22 melt viscosity results to similarly filled HI-10 melts were also conducted. The HI-10 melts showed higher shear viscosity results, independent of shear rate. However, within the HI-10 results, as the amount of SAN within the melt was increased, there was a noticeable decreases in the shear viscosity of the melt. This was attributed to the effective reduction in the amount of rubber particles within the melt. These rubber particles cause a resistance to flow for the polymer chains, therefore causing an increase in the viscosity of the melt.

The shear stress results of the GP-22 based WPC melt were found to be directly dependent on the amount of wood filler and temperature of the melt. Increases in shear stress were seen as the temperature decreased and the filler level increased. Both the GP-22 and HI-10/SAN formulations showed good overall agreement of the data from run to run. The HI-10 results showed a general decrease in the shear stress as the amount of rubber within the melt was lowered.

This research provides an initial examination into the use of a slit die rheometer in highly wood filled HDPE and ABS melts. The results of this study demonstrate that reasonable rheological results can be obtained using a slit die rheometer. This research also examines the rheological changes occurring in the melt for ABS/maple composites.

However, since the amount of rheological work on both the wood filled HDPE and ABS is very limited, there is a great deal of research that needs to be accomplished before a full understanding of flow properties can occur.

4.2 Future work

Since the slit die has been shown to be a reasonable tool for determining the rheological properties of WPC melts, further work into a full analysis of the pine-based melts is needed. It is expected that the pine results for shear viscosity and stress will be similar to maple based melts when there is a change in the pine filler amount, but there is minimal literature to confirm this result. It would also be of interest to see if similar changes in the shear stress and viscosity would be observed if the mesh size of the pine based composite was changed.

The research conducted in this study is also limited to wood and polymer composites with no added lubricants, coupling agents, modifiers or foaming agents. Since all commercial WPC melts will invariably contain some amount of these additives, it will be important for future work to examine the effects of these materials on the rheological properties. These additives will have pronounced changes on the rheological properties and should be closely examined.

APPENDIX A -

DETERMINATION OF WOOD PLASTIC COMPOSITE DENSITY

A.1 Introduction

Most rheological studies of the rheology of wood plastic composite (WPC) has concentrated around the use of off-line capillary die rheometers. Since this type of rheometer can have limitations when studying WPCs it is important to develop different techniques that will still be able to measure the rheological properties correctly but will be able to overcome some of the capillary dies problems. With the introduction of a rheological slit die as a measurement technique this problem is solved. However, since the slit die requires a mass flow rate to be calculated for calculating the properties, an accurate procedure for measuring the density of the wood plastic composite (WPC) is needed.

A.2 Literature

When doing the rheological tests using the slit die, it is important to correctly determine the density of the extrudate over the sixty-second sampling period. A similar method was used by Thorsteinsen et. al. (2003) to obtain the volumetric flow rate when examining unfilled PVC systems. This density value is then used for determining the volumetric flow rate (Q):

$$Q = \frac{m}{\rho} \tag{1}$$

where m is the mass flow rate and ρ is the density of the material. The volumetric flow rate allows for the calculation of the apparent shear rate ($\dot{\gamma}_a$) (Han, 1974):

$$\dot{\gamma}_a = \frac{6Q}{wh^2} \tag{2}$$

where w and h are the width and height of the slit die, respectively. The conversion of $\dot{\gamma}_a$ to obtain the true shear rate ($\dot{\gamma}$) is expressed as:

$$\dot{\gamma} = \left(\frac{2n+1}{3n}\right)\dot{\gamma}_a \tag{3}$$

where n is the Rabinowitsch correction factor and taken as $d \log \tau_w / d \log \dot{\gamma}_a$.

A.3 Measurement

In order to measure the density of the WPC correctly, ASTM D-2395 was followed for all of the samplings. This standard provides a standard test method for determining the specific gravity of wood and wood-base materials. Initial tests were carried out using Mode IV of the standard, to test for the specific gravity of the extrudate. A 500ml-graduated cylinder was used with a submersion of the sample into a water bath. This method did not allow for very accurate readings, since the human eye reads the water level and the graduated steps were very wide apart. Using this technique lead to a wide variety of results for the specific gravity of the WPC extrudates. Therefore, a better method of testing the specific gravity of the extrudate was needed.

The use of Mode II was determined to be the best method for this application. By placing a container filled with water on the balance (Figure A.1), the weight of the water changes as the buoyant force of the sample displaces a specific amount of water, and the weight of displaced water is equivalent to the volume of the water displaced. Since the container would not allow for a straight section of the extrudate to be tested, the need to compress the overall size of the extrudate had to be reduced. Therefore, a variety of different types of folding of the material were tested; a rolling, a folding and a zigzag method, with pictures of the three different methods shown in Figure A.2. The rolling method was eliminated since it was creating too many air pockets between the layers. In order to test the density of results of the remaining two methods, an experiment was conducted with 12 one-minute long samples for each of the two different methods. A random number generator was used to determine the order of the samples in a 24-minute sampling period. This order can be found in Table A.1. The density of the extrudates was measured following the ASTM D-2395 standard. A full listing of the densities of the extrudates is found in Table A.2.

A.4 Results and Discussion

With these densities, a small sample comparison t-test was run to determine if the two methods were producing the same values (Devore, 2000). The t-test indicated that the samples had a t-critical value of 0.484, and a P-value of 0.633. Since the null hypothesis states that the two populations are identical, when tested at significance levels of 0.01, 0.05 and 0.10, the null hypothesis is not rejected. These results are shown in Table A.3. Therefore, based on the results of the t-test, since the null hypothesis was not rejected, it was determined that the two methods produced identical densities for the melt. Since both methods produce the same result, the zigzag method was chosen over the folding method, as it is much easier for the operator to perform.

A.5 Conclusions

Since both the zigzag and folding method produce identical results, there is statistically no real advantage for using one method over the other. However, when the easy of use for the test operator is figured into the equation, the zigzag technique is much better match. Therefore, the use of the zigzag technique will be used on all future calculations. This will allow for consistent standard to be employed throughout the entire set of experiments.

A.6 References

ASTM D2395-97. “Standard Test Methods for Specific Gravity of Wood and Wood-Base Materials.” American Society for Testing and Materials.

Devore, J. L. Probability and Statistics for Engineering and the Sciences. 5th edition Duxbery. Pacific Grove, CA. 2000

Han, C.D. “On slit- and capillary-die rheometry.” Transactions of the Society of Rheology, 1974. Vol. 18.1, pp.163-190

Thorsteinsen, P., Hinrichsen, E.L. and Glomsaker, T. “A Dual Slit In-Line Die for Measuring the Flow Properties of S-PVC Formulations. Journal of Vinyl & Additive Technology. December 2003, Vol. 9, No. 4. pp. 188-197

A.7 Figures

Figure A.1. Measurement setup on balance

Folding

Zigzag

Rolling

Figure A.2. Different types of extrudate folding

A.8 Tables

Table A.1. Density Randomization

Run	Method	Run	Method
1	Zigzag	13	Folding
2	Folding	14	Folding
3	Folding	15	Zigzag
4	Zigzag	16	Folding
5	Zigzag	17	Folding
6	Zigzag	18	Zigzag
7	Zigzag	19	Zigzag
8	Folding	20	Folding
9	Folding	21	Zigzag
10	Zigzag	22	Folding
11	Folding	23	Zigzag
12	Zigzag	24	Folding

Table A.2. Density of samples

Run	Density (g/ml)	Run	Density (g/ml)
1	1.157	13	1.099
2	1.098	14	1.102
3	1.104	15	1.086
4	1.105	16	1.09
5	1.104	17	1.097
6	1.102	18	1.088
7	1.172	19	1.083
8	1.091	20	1.084
9	1.093	21	1.087
10	1.093	22	1.134
11	1.112	23	1.095
12	1.081	24	1.095

Table A.3. t-Test: Two-sample test

Significance Level = 0.10	*Variable 1*	*Variable 2*
Mean	1.104401	1.099935
Variance	0.000855	0.000166
Observations	12	12
Pooled Variance	0.000511	
Hypothesized Mean Difference	0	
df	22	
t Stat	0.484102	
P(T<=t) one-tail	0.316549	
t Critical one-tail	1.321237	
P(T<=t) two-tail	0.633098	
t Critical two-tail	1.717144	

Significance Level = 0.05	*Variable 1*	*Variable 2*
Mean	1.104401	1.099935
Variance	0.000855	0.000166
Observations	12	12
Pooled Variance	0.000511	
Hypothesized Mean Difference	0	
df	22	
t Stat	0.484102	
P(T<=t) one-tail	0.316549	
t Critical one-tail	1.717144	
P(T<=t) two-tail	0.633098	
t Critical two-tail	2.073875	

Significance Level = 0.01	*Variable 1*	*Variable 2*
Mean	1.104401	1.099935
Variance	0.000855	0.000166
Observations	12	12
Pooled Variance	0.000511	
Hypothesized Mean Difference	0	
df	22	
t Stat	0.484102	
P(T<=t) one-tail	0.316549	
t Critical one-tail	2.508323	
P(T<=t) two-tail	0.633098	
t Critical two-tail	2.818761	

APPENDIX B -

PARTICLE SIZE ANALYSIS

B.1 Introduction

The expanded use of wood plastic composites (WPCs) within the residential building industry has brought forward the need to accurately understand the rheology of the composite melts. Since the composition of the materials contained within the WPC melt can have a direct influence on the melt rheology, it is very important to determine the exact makeup of the materials within the melt. Therefore, the particle size of the wood filler needs to be measured so that the mesh size is verified.

B.2 Methods and Materials

In order for the slit die to correctly measure the rheology of the melt it is important for the smallest die dimension to be 40 times larger than wood particle size. Therefore, this slit die design was developed around the principles of continuum flow with a maximum wood flour particle height of 0.0635-cm (40-mesh). To validate the die continuum assumptions, the particle size of the dispersed wood filler was analyzed using an *in-situ* by using a scanning electron microscope (SEM) (Hitachi S-570).

To conduct the SEM measurements, a representative slit die extrudate containing 60% 40-mesh maple and 40% HDPE was randomly sampled and milled into two 5-mm cubes. A diamond microtone was then used to surface the cubes on one face normal to the flow direction. Each sample was sputtered with a 6.0-Å thick gold layer prior to examining. A series of forty SEM pictures were acquired using a magnification of 490x. The magnification was selected to balance edge detection of the wood particles and field of view. Since every picture was 1200 pixels wide by 1500 pixels high, ten random x-y coordinates within these ranges were assigned for each picture. These points were constant throughout the 15 randomly chosen pictures. At each one of these x-y coordinates the height of the particle was measured using UTHSCSA ImageTool (2002) software. The same calibration length was used for all of the pictures since the magnification of the images was constant throughout.

B.3 Results

After measuring the particle heights, it was determined that 136 points contained a particle, while 14 points did not. With the 136 points gathered from the SEM particle size analysis, it was important to determine what type of distribution the particles followed. The distribution of the wood flour particles within the melt is shown in Figure B.1. In order to determine if the particles were following a normal distribution, a Kolmogorov-Smirnov (K-S) goodness of fit test (Chakravarti, 1967) was performed on the particle distribution. In order to simplify the analysis of the K-S test, Analyse-It (2003) software was utilized on the data (Table B.1). Assuming a ß of 0.05, a p-value of <0.01 was obtained. This indicates that the particles do not follow a normal distribution as shown in Figure B.2, where the data does not follow the linear regression line.

Since the distribution of particles did not follow a normal distribution, it was determined that the particle heights followed a lognormal distribution (Figure B.3). The verification that the particles heights were following a lognormal distribution was completed following standard statistical techniques (Haan, 1977). Therefore, the mean particle height ($\bar{x}$) may be determined by first transforming the individual height data (x_i) using:

$$y_i = \ln x_i \tag{1}$$

and then computing the average as:

$$\bar{x} = e^{\bar{y}} = e^{\sum y_i/n} \tag{2}$$

where n = total number of samples. By transforming the particle heights using equation (1), the new values can be checked to see if they follow a normal distribution. In order to test this hypothesis, a K-S goodness of fit test was applied to the transformed samples using Analyse-It software. Assuming a ß of 0.05, a p-value >0.15 was achieved, with complete statistical results shown in Table B.2. The K-S test states that for the null hypothesis to not be rejected, a high p value must be obtained. The ability of the data to fit the linear regression of the K-S test is seen in Figure B.4.

Since the particle values were determined to follow a lognormal distribution, the average transformed mean value of 3.29 μm was transformed back into the original domain, resulting in an average particle height of 25.6 μm. Therefore, to validate that the slit dimensions followed the continuum assumptions, the mean particle height was multiplied by 40 to yield a minimum of 1.02-mm. This value is well below the 5.0-mm slit height and does not violate the continuum requirements.

B.4 Conclusions

Since this slit die design used to measure the rheology of WPCs has never been used on these types of filled systems, it is important to make sure that the design is correct. The verification of the slit die design is confirmed by determining the average particle height of the wood flour within the melt. Using a developed SEM technique it has been shown that the die design is well within the restrictions of the continuum assumptions and will allow for accurate results to be achieved when it is used to quantify the rheological properties of the WPC melt.

B.5 References

Analyse-It. Version 1.71. December 11th, 2003. Analyse-it Software Ltd.

Chakravarti, Laha, Roy. "Handbook of Methods of Applied Statistics." Volume 1. John Wiley and Sons, pp. 392-394, 1967.

Haan, C.T. Statistical Methods in Hydrology. The Iowa State University Press. Ames, Iowa. 1977

University of Texas Health Science Center at San Antonio. UTHSCSA ImageTool Version 3. Feb. 2002

B.6 Figures

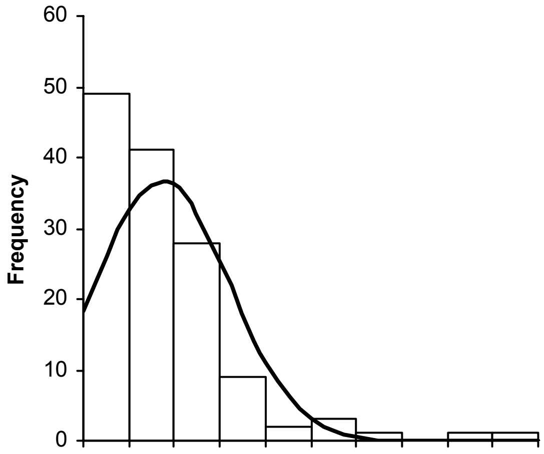

Figure B.1. Distribution of particle heights

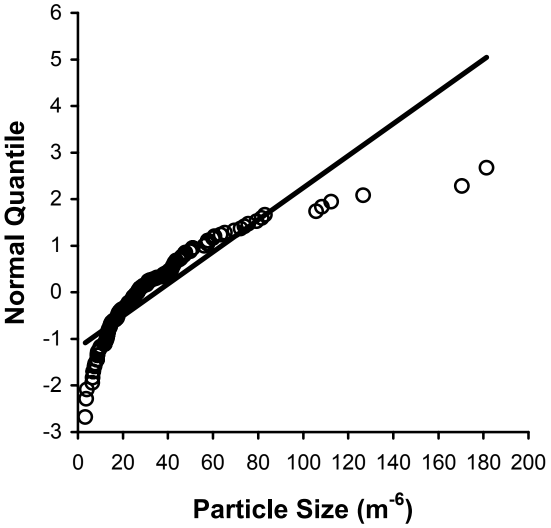

Figure B.2. Kolmogorov-Smirnov fit of normal data

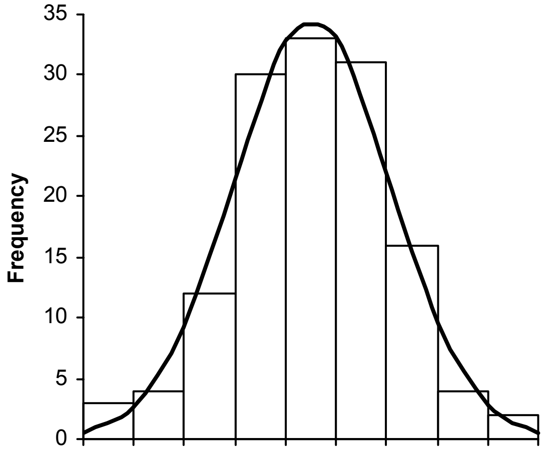

Figure B.3. Lognormal distribution of particle heights

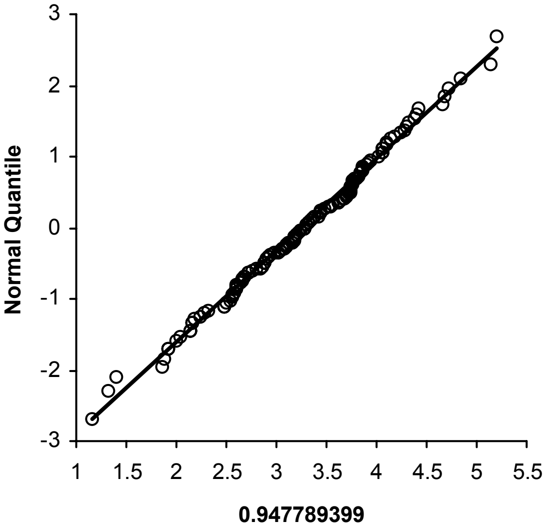

Figure B.4. Kolmogorov-Smirnov fit of transformed data

B.7 Tables

Table B.1 Normalized Data Results

n	135	
Mean	34.649	
95% CI	29.694 - 39.603	
Variance	847.1349	
SD	29.1056	
SE	2.505	
CV	84%	
Median	26.56	
96.2% CI	22.530 - 31.060	
Percentile		
2.5th	4.988	
25th	14.89	
50th	26.56	
75th	43.46	
97.5th	121.002	
	Coefficient	p
Kolmogorov-Smirnov	1.7159	< 0.01
Skewness	2.3839	<0.0001
Kurtosis	7.9084	<0.0001

Table B.2 Normalized Data Results

n	135
Mean	3.259
95% CI	3.127 - 3.390
Variance	0.5973
SD	0.7729
SE	0.0665
CV	24%
Median	3.279
96.2% CI	3.115 - 3.436

Percentile	
2.5th	1.58
25th	2.701
50th	3.279
75th	3.772
97.5th	4.794

	Coefficient	p
Kolmogorov-Smirnov	0.6106	> 0.15
Skewness	-0.1305	0.5222
Kurtosis	0.0009	0.8629