Characterizing The Flow Of Concentrated Slurries and Polymer Melts Using Percolation Theory Based Functions

Gregory A. Campbell, Castle Associates, Jonesport, Maine 04649
swcgac@maineline.net
Cell: 207 271 7730

Michael E. Zak, Xerox

Abstract

The production of many polymers such as PPO is carried out as a two phase suspension in essentially a Newtonian carrier fluid. This paper brings together three percolation based theories that provide insight into the effect of fillers on the rheological response of concentrated Newtonian fluid slurries to shear rate. First, a previously proposed limiting, zero shear, viscosity model based on percolation theory concepts is reviewed. Second, all Newtonian fluid based slurries that have a high concentration of filler become shear thinning at some shear rate. A new theory is reviewed that correlates the power-law constant, \( n \), to cluster formation of the fillers suspended in the fluid. Third, this cluster percolation based rheological analysis is then extended in this paper to a newly proposed model for the calculation of the ratio of infinite shear, \( \eta_\infty \), to the zero shear viscosity, \( \eta_0 \), as a function of the power-law. Using literature data and a modification of this theoretical treatment, it is demonstrated that, \( \eta_\infty / \eta_0 \) the viscosity ratio measurements correlate well with the power-law. Unfilled polymers also can reach the second Newtonian plateau and that has been seen to be related to the power law, \( n \), of the polymer melt.

1. Introduction

The general relationship for the viscosity of slurries is diagramed in Figure 1. At very low shear rates, the viscosity acts in a Newtonian manner being independent of the shear rate. The apparent viscosity often decreases as the shear rate is increased with the viscosity transitioning into the power law region. The power-law region found in Figure 1 is indicative of this rheological response. For any given material, the power-law is usually reported to be consistent regardless of the rheometer used: capillary, cone and plate, bob and cup or parallel plates. The slurry at high shear rates often becomes Newtonian again with increased but at a much lower value, “infinite” shear viscosity, than in the low shear rate Newtonian plateau. This paper presents percolation theory based models that seem to address these three parts of the viscosity vs. shear rate curve.

For simple, one-velocity component flow, the viscosity-power law relationship is:

\[ \eta = k |\dot{\gamma}|^{n-1} \]  

(1)

where \( \eta \) is the viscosity, \( |\dot{\gamma}| \) is the one component shear rate (the absolute value brackets are used because viscosity is positive definite) and \( n \) is the power-law constant. If \( n = 1 \), then \( k \), the consistency, is the shear rate independent viscosity.
Figure 1. Polymer viscosity vs. shear rate response.

As pointed out by [Campbell, Zak, Radhakrishnan, (2016)], when four grades of calcium carbonate were evaluated in a capillary rheometer and the percolation concentration, \( \phi_c \), and the maximum concentration, \( \phi_m \), were found, the typical power law versus filler volume fraction response was found as in Figure 2. The percolation threshold concentration changed with particle size. The largest two particle sizes showed essentially the same threshold volume fraction, 0.173. This value was close to the theoretical value of 0.16. For the 3.0 µm Camel-WITE particles, and then again for the 0.7 µm CAL-ST particles, the threshold concentration shifted to a higher concentration with a decrease in particle size.

2.1 Zero Shear Viscosity

One of the goals of this paper is to present rheological functions for the three zones of the viscosity of a filled system like that in Figure 1 based on percolation theory cluster dynamics. At low to very low shear rates, most particulate filled slurries exhibit Newtonian behavior. As the shear rate increases the Newtonian behavior at low shear often transitions to shear-thinning behavior at higher shear rates. These characteristics are considered here to be related to the change in dynamics of the clusters in the slurry as predicted by percolation theory. The mechanism and theory relating the power law “n” for the shear-thinning behavior of concentrated suspensions to cluster development is reviewed here in section 2.2 and was previously developed, [Campbell, Zak, Radhakrishnan, (2016), Zak, (1994), Radhakrishnan, (2002)]. A preliminary description relating this percolation based analysis to filled polymers [Campbell, Zak, Radhakrishnan, and Wetzel, (2016) and Wetzel, Pettitt, and Campbell, (2016)].

It has been shown [Segré and Silberberg, (1962), Karnis, Goldsmith Mason, (1966-1), Karnis, Goldsmith and Mason, (1966-2), Cox and Mason, (1971), Gauthier, Goldsmith and Mason, (1971), Park et.al (1988), Hoffman, (1972), Graham and Bird, (1984), Graham and Steele, (1984), Gadala-Maria and Acrivos, (1980), Husband and Gadala-Maria, (1987), Parsi and Gadala-Maria, (1987), B. J. Ackerson, (1990), Petit and Noetinger, (1988), Bossis and Brady, (1984), Brady and Bossis, (1985), Bossis and Brady, (1987), Phillips, Brady and Bossis, (1988), Durlofsky, Brady and Brenner, (1958)] that macroscopic structures were present as concentrated suspensions were deformed. These macroscopic clusters of agglomerated particles had a significant effect on the behavior of the suspension. Experimental evidence [Segré and Silberberg, (1962), Karnis, Goldsmith Mason, (1966-1),10Hoffman, (1972),18] showed that there was no motion amongst the particles within these clusters. This led to the new hypothesis that the power law region of the viscosity curve reflected the change in volumetric energy dissipation related to the concentration of the filler and the shear rate, Campbell, Zak and Radhakrishnan, (2016) when the shear rate increased to a point that the rheological response was no longer Newtonian.

Before discussing the slurry power law response, first the low shear rate Newtonian plateau is addressed, it was previously proposed by Campbell and Forgacs, (1990) that at low shear rates, particles in the “infinite” cluster had time to rearrange, allowing the cluster to deform as a result of the imposed flow field shear rate. The particles rearranged themselves by moving into existing holes within a cluster or closest neighbors [Campbell and Forgacs, (1990)]. This allowed for imposed stress to be transferred throughout the suspension and for the fluid to

Table 1. Calcium carbonates of different particle sizes
with percolation and maximum packing values.

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Nominal Avg. Particle Size</th>
<th>( \phi_c )</th>
<th>( \phi_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Omyacarb 21</td>
<td>21 µm</td>
<td>0.1726</td>
<td>0.5930</td>
</tr>
<tr>
<td>Omyacarb 10</td>
<td>10 µm</td>
<td>0.1732</td>
<td>0.6061</td>
</tr>
<tr>
<td>Camel-WITE</td>
<td>3 µm</td>
<td>0.2006</td>
<td>0.5360</td>
</tr>
<tr>
<td>CAL-ST</td>
<td>0.7 µm</td>
<td>0.2327</td>
<td>0.6732</td>
</tr>
</tbody>
</table>

A typical result for the power law function of calcium carbonate slurry in a polyol is found in Figure 2. The data indicate that there was a linear relationship between the power law and the concentration to the \((-2/3)\) power. Since the volume fraction to the \((-2/3)\) power could be the surface to volume ratio, this may imply that the power law is a function of some surface area related to the particles.

Figure 2. Power law vs. calcium carbonate filler concentration, from Zak thesis [ Zak, (1994)].

2. Theory Development

The zero shear and power-law theories have been presented elsewhere and are reviewed here to provide a foundation for the development of the infinite shear to zero shear viscosity ratio analysis.
perform work on all of the particle and container surfaces, thus yielding a Newtonian viscosity:

\[
\eta_r = \left( \frac{\phi_m - \phi_c}{\phi_m - \phi} \right) - 1
\]

where \( \eta_r \) is the Newtonian viscosity ratio, \( \phi_m \) is the Maximum packing concentration, \( \phi_c \) is the Percolation concentration and \( \phi \) is the Filler concentration. This was similar to the idea of a characteristic time for a material put forth by Heyes and Melrose, (1989). Their characteristic time was a measure of the time required for significant local structure change to occur in the material.

### 2.2 Power-Law Index, \( n \)

As the shear rate is increased, the concentrated slurry will begin to act as a power-law fluid as illustrated in Figure 1. The hypothesis presented next relates the power law to the slurry cluster structure change in response to the shear rate. When the whole suspension can dissipate energy, the behavior is Newtonian. As the concentration increases above some critical concentration for “infinite” cluster formation, macroscopic clusters form and the volume of these clusters increases with the particle concentration. At very low shear rates the slurry has a Newtonian response, the particles in the clusters can respond to the shear stress. There is then a transition to shear-thinning behavior above zero shear rates which is proposed to be due to not allowing time for “infinite” cluster structure rearrangement.

It follows that the power-law index, \( n \), which represents the fraction of the slurry volume that is dissipating energy, [Campbell, Zak and Radhakrishnan, (2016)], decreases from its Newtonian value of unity towards zero as the clusters grow and the maximum packing fraction is approached; see the experimental data for calcium carbonate presented in Figure 2. As the maximum packing fraction is approached, it is proposed that the volume available for energy dissipation decreases toward zero. This analysis only applies when the concentration and the shear rate combine to produce pseudo-plastic behavior that can be described by a single power-law index.

Therefore, it was proposed [Campbell, Zak and Radhakrishnan, (2016)] that it is the loss of sheared surface area upon which the fluid can perform work that is responsible for the apparent decrease in the viscosity. Using Green's theorem, one can look at the power law “\( n \)” as representing loss in volume within the slurry that is capable of viscous energy dissipation. This hypothesis is an alternative to past analyses [Heyes and Melrose, (1989), Einstein, (1906), V. Vand, (1948), Simha, (1952), Frankel and Acrivos, (1967), Hinch, (1977), Tanaka, and White, (1980), Batchelor, (1977), van de Venn and Hunter, (1977), Jarzebski, (1981)] where the whole volume of the suspension was taken to be dissipative and was usually analyzed as a Newtonian system.

The definition developed in [Campbell, Zak and Radhakrishnan, (2016)] of the power-law index based upon this model is the ratio of (1) the viscous dissipation of energy in the volume of the suspension minus that volume occupied by the non-dissipative clusters, to (2) the dissipation that would occur if the fluid that is dissipating energy could occupy the total volume available. The approach developed here may be taken as an extension of the approach of those analyses that take the interstitial fluid in clusters into account when calculating the zero-shear suspension viscosity, [Wildemuth and Williams, (1984), Vand (1948), Graham, et al., (1984), and Hoffman, (1974)].

The power-law index definition is then:

\[
\int_{v-c}^{v-v} \frac{\tau_{ij} dV}{\int_{v}^{v} \tau_{ij} dV}
\]

This general model for the power-law index predicts \( n = 1 \) when the volume of the non-deformable clusters \( V_c = 0 \), and it predicts that \( n \) will approach zero in the limit when \( V_c \) reaches \( V \). The definition is applicable to all shear fields and this leads to the assumption [Campbell, Zak, Radhakrishnan, (2016)] that the power law should be the same regardless of the rheometer type used. In order to evaluate the utility of this model for prediction of the power-law index, one must quantify the non-dissipative volume and evaluate the integrals.

When this investigation was initiated, there was a lack of quantitative data in the literature for the location and amount of structure formation in Couette, cone and plate, and other linear flow viscometers, since it would be extremely difficult to relate experimentally the power-law index for those cases to the dispersed non-deformable clusters. Experiments by Karnis et al. [Karnis, Goldsmith Mason, (1966-1), Karnis, Goldsmith and Mason, (1966-2)] indicated that there was non-deforming central plug in tube flow and [Altobelli, Givler and Fukushima(1991)] with nuclear magnetic resonance imaging supported the results of Karnis et al. as they also demonstrated that there was a central non-deforming structure in tube flow, that being the core cluster in Poiseuille flow. From a visual inspection of the velocity profiles of Karnis et al. [Karnis, Goldsmith Mason, (1966-1),] it was proposed to use a Bingham model of the stress tensor to represent the flow field for modeling the dissipative region [Campbell, Zak, Radhakrishnan, (2016), Zak, (1994), Radhakrishnan, (2002)]. This choice hypothesized that the behavior was Newtonian in the dissipative region as proposed by [Campbell and Forgacs]
(1990)] and approached “perfect” plug flow in the
organized cluster region.

The denominator of expression, equation 4, for the
power-law index was defined for a suspension flowing
through a tube without a central core [Campbell and
Radhakrishnan, (2016), Zak, (1994), Radhakrishnan,
(2002)]. This corresponded to a Bingham fluid flowing
with a yield value of zero, for which the velocity profile
simplified to the parabolic Newtonian expression. The
pressure drop for both flow cases (i.e., that with a central
core and that without a central core) and the tube
geometry were here assumed to be equal, a key
assumption. The defining expression for the power-law
index was written as:

$$n = \frac{\int \tau_{ij} d_{ij} r dr}{\int R_{ij}^* d_{ij}^* r dr}$$

(4)

The * indicates that these terms represent the zero
core size expression and the corresponding flow field.
The results of the $\theta$ and $z$ direction integrals cancelled out.
The upper integral in this analysis was over the annulus
where there was enough shear stress induced by the local
shear rate to deform the local clusters in a Newtonian
response as discussed previously [Campbell and Forgacs,
(1990)]. Evaluating the integrals between $R_c$, the core
radius, and the tube radius, $R$, using the Bingham
viscosity model and cancelling like terms, the expression
for the power-law index was determined as:

$$n = 1 - \frac{4}{3} \varepsilon + \frac{1}{3} \varepsilon^4$$

(5)

where:

$$\varepsilon = \frac{R_c}{R} \frac{\tau_y}{\tau_{rc}} (r = R)$$

(6)

The expression, equation 5, is consistent with

$$\tau_{rc} = \tau_y \text{ for } R \leq R_c$$

and

$$\tau_{rc} = \mu_b \frac{dU_z}{dz} + \tau_y \text{ for } R > R_c$$

resulting from

The upper and lower limits of $n$ are correct, equation 5.
When there was no plug present, $\varepsilon = 0$. Newtonian flow
was predicted, $n = 1$. As the core size approached the size
of the tube, $\varepsilon \rightarrow 1$, the volume for dissipation went to zero
and $n$ approached zero in the limit as well, $R_c$ approaches
$R$, per Figure 3.

![Figure 3. Slurry Velocity Profile as a function of filler
concentration (concentrations: 1 less than
percolation, 2 and 3 concentrations increasing
above percolation) [Campbell, Zak and
Radhakrishnan, (2016)].](image)

The validity of equation for $n$ was substantiated
by the fact that $\varepsilon = 1$ was the only real root. As pointed
out previously [Campbell, Zak and Radhakrishnan,
(2016)] perhaps the most common and widely used non-
Newtonian model for pseudoplastic fluids is the empirical
Ostwald and de Waele's power law. In contrast, what we
propose here is a physics based theory for shear thinning
of at least Newtonian fluid based slurries. At any shear
rate where the core cluster is detected, it, $n$, is a
thermodynamic property of the slurry because the non-
dissipating cluster volume no longer dissipates energy at
that shear rate [Campbell, Zak and Radhakrishnan,
2 reflects the dissipation in the annulus. As the shear rate
is increased the central core will reach a limit, maximum
cluster size, which is a function of the filler concentration,
[Campbell, Zak and Radhakrishnan, (2016) and
Radhakrishnan, (2002)]. At this point the flow becomes
Newtonian again and this is usually defined as the infinite
shear viscosity for the slurry, $\eta_\infty$. In the next section, an
expression is developed that as far as the authors have
found is the first attempt to relate the infinite shear
viscosity, $\eta_\infty$, of a slurry to the non-dissipation volume in
a concentrated slurry through the power-law, $n$.

2.3 Infinite Shear to Zero Shear Viscosity Ratio

For this phase of the analysis the model is again
based on tube flow because the cluster volume can be
functionally related to the non-deforming central core of
slurries through $R_c / R$. Inherent in this assumption is the
hypothesis that the volume of the non-deforming clusters
is independent of the velocity field. Tube flow is used because the non-deforming cluster is measurable as the central core of the flowing slurry. By using the same tubular flow based analysis for the power-law and the viscosity ratio, \( \eta_{r,\infty}/\eta_{r,0} \) it follows that the power-law region and the viscosity ratio theoretical models for the respective regions in Figure 1 will be related through the same parameter \( \varepsilon \).

The analysis starts with the method developed by Brenner (1958) to define relative viscosity:

\[
\eta_r = \frac{\int p_n u_idS}{\int p_n^0 u^0_idS} = \frac{\sum S_i}{\sum S_i} \]  

(7)

Here \( p_n \) is the outer normal traction on the surface and \( u_i \) was the velocity and \( S \) is the surface area that is dissipating energy, \( S_c \) is the surface area of the particles in the slurry. The expression developed by Brenner (1958) for the relative zero-shear viscosity, equation 7, above, provided a way to write the relative infinite-shear viscosity, \( \eta_{r,\infty} \). The suspending fluid could perform work on the container surfaces, \( S_m \), the surfaces of the non-dissipative clusters, \( \sum S_i \), and the surfaces of the single particles and those clusters that were able to deform, \( \sum S_j \).

Relative to the suspending fluid, the infinite-shear viscosity was:

\[
\eta_{r,\infty} = \frac{\int p_n u_idS}{\int p_n^0 u^0_idS} = \frac{\sum S_i}{\sum S_i} \]  

(8)

Combining equations 7 and 8:

\[
\frac{\eta_{r,\infty}}{\eta_{r,0}} \rightleftharpoons \frac{\int p_n u_idS}{\int p_n^0 u^0_idS} = \frac{\sum S_i}{\sum S_i} \]  

(9)

\( \infty \) represented the fluid stresses in the infinite-shear case, and \( * \) represented the fluid stresses for the zero-shear flow case. Equation 9 was similar in form to the definition for the power-law index, equation 4. \( \eta_{r,\infty}/\eta_{r,0} \) was the ratio of the limits of energy dissipation. The power-law index mapped how the energy dissipation changed from the upper limit, expressed by \( \eta_{r,\infty} \), to the lower limit, expressed by \( \eta_{r,0} \). The key difference was that the structure and dissipation in the suspension changed as a function of shear rate as the shear rate progressed from the lower zero-shear region to the upper infinite-shear region. However, since the ratio \( \eta_{r,\infty}/\eta_{r,0} \) represented those two regions of energy dissipation and the limiting power-law index represented the maximum amount of change between these two extremes, a possible relationship between \( n \) and \( \eta_{r,\infty}/\eta_{r,0} \) was investigated.

The simplified, volume-based viscous dissipation of energy expression is:

\[
E_v = \int \mu \gamma^2 dV \]  

(10)

for a Newtonian fluid. The suspension behaved as a Newtonian fluid in the zero-shear and infinite-shear regimes. The shear rate for a Newtonian fluid is:

\[
\dot{\gamma}_N = -\frac{\Delta \Pr}{2\mu L} \]  

(11)

The shear rate for a Bingham fluid is:

\[
\dot{\gamma}_B = -\frac{\Delta \mu'}{2\mu_b L} (r - R_c) \]  

(12)

In the zero-shear case, \( \mu \) acted over the whole volume available for energy dissipation. The zero-shear viscosity \( (\eta_{r,0}) \) was also calculated over this volume. However, in the case of a Bingham model description of a partial plug velocity profile, \( \mu_b \) acted only in the dissipation region, in the same manner as for zero-shear case regarding filler concentration, \( \varepsilon \). Therefore, \( \mu_b \) was actually larger than \( \mu \) since the calculation of \( \eta_{r,0} \) spread \( \mu_b \) over the whole capillary volume. For this analysis, \( \mu_b \) was assumed to be equal to \( \mu \), as a first approximation, thus a “Newtonian” assumption. This meant that a suspension with the same viscosity was dissipating energy in the zero-shear region and the infinite-shear region. The actual viscosity of that part of the suspension dissipating energy would be derived from the concentration of solids. The volume for dissipation and the shear rate had changed between the zero-shear and infinite-shear cases. The actual viscosity of that part of the suspension dissipating energy would be derived from the concentration of solids.

This lead to the following expression for the ratio of the zero-shear viscosity to infinite-shear viscosity:

\[
\frac{\eta_{r,\infty}}{\eta_{r,0}} = \frac{\int_R^r \mu \left[ \frac{\Delta \mu'}{2\mu_b L} (r - R_c) \right]^2 rdr}{\int_0^r \mu \left[ \frac{\Delta \mu}{2\mu L} (r) \right]^2 rdr} \]  

(13)

for flow through a capillary. The second assumption was that the shear stress was the same in both cases.
Therefore, the capillary geometries and the pressure drops were the same. The resulting expression for the viscosity ratio was:

\[
\frac{\eta_{r,e}}{\eta_{r,0}} = 1 - \frac{8}{3} \varepsilon + 2 \varepsilon^2 - \frac{1}{3} \varepsilon^4 \tag{14}
\]

This expression as stated above is a Newtonian approximation. However, all of the flow visualization date [Zak (1994), Karnis, Goldsmith Mason, (1966-1), Karnis, Goldsmith and Mason, (1966-2), Radhakrishnan, (2002) and Altobelli, Givler and Fukushima, (1991)] presented a velocity profile that can be interpreted as Bingham like flow. The following first order correction is proposed for a Bingham approximation of equation 14, [Zak, (1994)]:

\[
\frac{\dot{\gamma}_N}{\dot{\gamma}_B} = \frac{R}{R - R_C} \tag{16}
\]

This expression equation 16 is than proposed to scale equation 14 to better represent the Bingham flow experimentally observed as follows is equation 17:

\[
\frac{\eta_{r,e}}{\eta_{r,0}} = \left(1 - \varepsilon \left[1 - \frac{8}{3} \varepsilon + 2 \varepsilon^2 - \frac{1}{3} \varepsilon^4\right]\right) \tag{17}
\]

Based on the hypothesis and assumptions presented in the first paragraph in this section, simultaneously evaluating equations 5 and 17 using appropriate values of \( \varepsilon \) should relate the ratio of infinite shear to zero shear viscosity, \( \eta_{r,e}/\eta_{r,0} \), to the power law \( n \). This proposal will be tested in the next section.

3. Data and Discussion

3.1 Power-law Evaluation

Using equation 2 a set of zero shear viscosity data are presented in Figure 4. These are the data that were used in the investigation of the development of the central cluster analysis reported in [Zak, (1994), Radhakrishnan, (2002)]. The slurry batch relative viscosity data was developed in Ubbelohde capillary viscometers [Radhakrishnan, (2002)] and was fitted to the percolation theory based viscosity model of Campbell and Forgacs, (1990) (Equation 2). The Campbell and Forgacs, (1990) model contains two parameters - the maximum packing fraction \( \phi_m \) and the critical percolation threshold \( \phi_c \). The parameters were evaluated from the data using linear regression. The obtained values were \( \phi_c = 0.18 \) and \( \phi_m = 0.61 \). As seen in Figure 4, the experimental data are in excellent agreement with the percolation-based model in this concentration range. Also the value obtained for \( \phi_m \) is very close to the low shear maximum packing fraction of 0.63 and the \( \phi_c \) obtained is close to the theoretical percolation threshold of 0.154. It is interesting that this model also provides a good fit even below the percolation concentration.

3.2 Power-law Evaluation

Zak (1994) converted the data from Karnis, et. al. and Altobelli, et al. [Karnis, Goldsmith Mason, (1966-1), Karnis, Goldsmith and Mason, (1966-2) and Altobelli, Givler and Fukushima, (1991)] into the form needed to evaluate the utility of equation 5. This is the first time that the experimental data from these papers are used to test this power-law,\( n \), cluster based theory. The converted data as plotted in Figure 5, along with the theory line from equation 5. It is apparent that the power-law theory and the predictions from the plug size reported in the literature data are in agreement over a wide range of plug sizes.
What follows is a short review [Campbell, Zak and Radhakrishnan, (2016)], of the challenge to relate the size of the non-dissipation cluster to the power law traditionally determined using the pressure drop across the length of the tube. Data on the core to capillary ratio and the corresponding values of the power-law index were needed in order to verify if equation 5 also predicted the power-law traditionally evaluated using pressure drop in tube flow. Experiments were carried out using PMMA beads flowing in a tube such that the velocity profile and the traditional power law index “n” calculated from the pressure drop across the tube were evaluated simultaneously [Campbell, Zak and Radhakrishnan, (2016), Zak, (1994), Radhakrishnan, (2002), Wetzel, (2016) and Wetzel, Pettitt, and Campbell, (2016)]. The $R_c/R$ values were used to calculate the power law as predicted in equation 5 to verify if the “infinite cluster” the central plug prediction correlated with the traditional power-law.

The suspending fluid was a mixture of Triton X-100 (a non-ionic surfactant) and an aqueous solution of ZnCl$_2$ which produced a neutrally buoyant suspension. The filler particles were Diakon® LS-600 polymethylmethacrylate spheres from ICI Acrylics, Inc., and polystyrene divinyl benzene spheres from Duke Scientific Corporation. A PMMA tube was used to observe the suspension flow. The suspending fluid, the PMMA beads, and the PMMA tube had the same refractive index so they did not reflect the laser light. The laser had enough UV content to cause the polystyrene particle to glow. A video camera was used to monitor the velocity of the particles and this video was analyzed to quantify the velocity as a function of the distance across the center of the tube.

3.2. Experimental Procedures

The velocity profiles of the suspensions were measured by videotaping the flow and tracking the polystyrene tracer particles as they flowed through an acrylic tube. To illuminate the tracers a sheet of laser light was directed through the center of the tube, parallel to the tube axis. In order to be able to see the tracer particles, a microscope was used to magnify them. The video camera was placed in the photo port of the microscope. After starting a given trial, the pressure drop increased for a given amount of time before reaching a steady state. When the pressure drop became steady, the video tape was started for recording the polystyrene particle migration and the pressure drop was recorded twelve times. The next part of the analysis was the measurement of point velocities. This was done using HL++ image analysis software. The VCR and monitor assembly was hooked up to the computer and the image analysis software was used to grab still pictures from the recording.

Plug size data were used to develop the theory line in Figure 6 and superposed in the same plot are the power-law values calculated in a conventional manner using the pressure drop at that experimentally developed plug size. It should be noted that this theory has no adjustable parameters. The theory line and the power-law data show excellent agreement as plotted in Figure 6. More details of the experiments and analysis can be found in [Campbell, Zak and Radhakrishnan, (2016), Zak, (1994), Radhakrishnan, (2002), Campbell, Zak, Radhakrishnan, Wetzel, (2016), Wetzel, Pettitt, and Campbell, (2016)].

3.3 Power-law filler concentration dependence
The equation used to represent the power-law after the critical percolation concentration in Figure 2 was developed by Zak [Zak, (1994)]:

\[ n = \frac{\left( \frac{\phi}{\phi_m} \right)^{2/3} - 1}{\left( \frac{\phi_c}{\phi_m} \right)^{2/3} - 1} \]  

(18)

Using this percolation based function, the data presented in the previous graph, Figure 6, can be correlated to a surface to volume ratio for the filler, exponent (2/3), in the slurry using equation 18 as seen in Figure 7.

![Figure 7. Power law constants from two data sets](image)

From these data and their good fit, it is proposed that the power law rheological response is a filler concentration dependent function where a surface area of the filler is a dominant factor as indicated by the (2/3) power of the concentration. To reiterate, it has generally been observed in the literature that the power law measured in traditional rheometers is the same regardless of the flow field, capillary, cone and plate, or parallel plate rheometers. Therefore, this analysis would be expected to apply to these differing rate fields when the cluster volume can be quantified. It also follows that if the power law “n” is known, then the volume fraction of the non-dissipating clusters can be found for all of these systems using equation 5.

3.4 Infinite Shear to Zero Shear Viscosity Ratio

At this point in the paper, the first two zones in Figure 1 have now been modeled and the models compared with experimental data. The theory developed earlier for the third zone, infinite shear viscosity, will now be compared to data which relates the infinite/zero shear viscosity to the power law. The data from sources that provided the power law and the ratio of the Infinite to Zero Shear viscosity were collected from the literature, Table 2.

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Particles and sizes</th>
<th>Suspending Fluid</th>
<th>Rheometer Type</th>
<th>Volume Fraction Range and ( \eta_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. Castillo and M.C. Williams(1979)</td>
<td>Coal, &lt;62 µm</td>
<td>Chlorinated Biphenyl or Glycerin</td>
<td>Weissenberg cone and plate</td>
<td>0.2-0.6, ( \phi_0 = 0.68 )</td>
</tr>
<tr>
<td>W.-Y. Chiu and T.-M. Don(1989)</td>
<td>Salt, 50 and 230 µm</td>
<td>Hydroxy l Terminated Polytetra diene</td>
<td>Concentric cylinder</td>
<td>0.6 by weight, ( \phi_0 = 0.62 )</td>
</tr>
<tr>
<td>C.G. de Kruif, E.M.F. van Iersel and A. Vrij(1985)</td>
<td>Silica, 78 nm</td>
<td>Cyclohexane</td>
<td>Deer double-cylinder Couette</td>
<td>0.0006 - 0.6, ( \phi_0 = 0.63 ) or 0.7</td>
</tr>
<tr>
<td>H. Goto and H. Kom(1955)</td>
<td>Polystyrene 84 and 398 µm</td>
<td>Ethylene and Propylen e Glycol</td>
<td>Capillary</td>
<td>0.2, ( \phi_0 = 0.62 )</td>
</tr>
<tr>
<td>S.H. Maron and R.J. Belner(1955)</td>
<td>Butadiene-Styrene Latax, 1216 A</td>
<td></td>
<td>Capillary</td>
<td>0.293 - 0.564, ( \phi_0 = 0.84 )</td>
</tr>
<tr>
<td>S.H. Maron and S.H. Fok(1955)</td>
<td>Butadiene-Styrene Latax, 1388 A</td>
<td></td>
<td>Capillary</td>
<td>0.299 - 0.6017, ( \phi_0 = 0.84 )</td>
</tr>
<tr>
<td>S.H. Maron and A.E. Levy-Pascal(1955)</td>
<td>Polychloroprene, a Neoprene Latax, 1100 A</td>
<td></td>
<td>Capillary</td>
<td>0.2393 - 0.5115, ( \phi_0 = 0.84 )</td>
</tr>
<tr>
<td>S.H. Maron and A.W. Sisko(1957)</td>
<td>Butadiene-Styrene Latax, 1216 A</td>
<td></td>
<td>Capillary</td>
<td>0.293 - 0.564, ( \phi_0 = 0.84 )</td>
</tr>
<tr>
<td>S. Yao and T. Matsumoto(1987)</td>
<td>Styrene-divinylben zene, 110 nm</td>
<td>Diethyl phtha-late</td>
<td>Weissenberg cone and plate</td>
<td>0.05 - 0.30, ( \phi_0 = 0.62 )</td>
</tr>
<tr>
<td>Krieger(1972)</td>
<td>Mono disperse latex 0.155 to 0.220 µm</td>
<td>Triton X-100 Water</td>
<td>Capillary Cone and Plate Couette Parallel Plate</td>
<td>&lt;0.55</td>
</tr>
</tbody>
</table>

The \( \eta/ \eta_0 \) data from these sources are plotted in Figure 8 as a function of the literature reported power-law, n, from the same publication. Consistent with the earlier proposal regarding the power-law, n, regardless of the rheometer.
In order to determine the utility of the proposal made above, equations 5, 14 and 17 were related using values of \( Rc/R \) from 0.0 to 1.0 in order to get corresponding power-law, \( n \), and the associated viscosity ratio, \( \eta_c/\eta_0 \). The resulting calculations for the power-law \( n \), the predicted Newtonian based \( \eta_c/\eta_0 \) and the Bingham \( \eta_c/\eta_0 \) are found in columns 2 through 4 in Table 3.

The data in Figure 9 were replotted from Figure 8 with the Newtonian and Bingham theories developed above, equations 14 and 17 added to the graph. Reiterating, as reported in Table 2 the data were collected using capillary, cone and plate, parallel plate, coquette, and cup and bob rheometers. It is apparent that the data regardless of the rheometer type fall as a continuous function. This supports the hypothesis that was proposed in the previous work [Campbell, Zak and Radhakrishnan, (2016)] and in Section 2.1 that the fraction of the system that represents non-deforming clusters is independent of the shear field. Further, the data strongly suggest that there is a consistent relationship between the viscosity ratio, \( \eta_c/\eta_0 \) and the power law, which has been previously shown to represent the fraction of slurry that is dissipating energy, regardless of the type of particle or the type of rheometer. It is apparent that the Newtonian function, equation 14, has the generally correct shape, but does not conform to the data very well, it consistently under predicts the rate of decrease in viscosity ratio as a function of the power-law. Using the Newtonian theory, essentially all values of the power-law, the predicted \( \eta_c/\eta_0 \) decreased much more slowly than the reported data. However, the Bingham approximation has a more correct trend. The Bingham approximation, equation 17, does provide a better “fit” than the Newtonian function particularly at high power-law values and at small power-law values; however, it still under predicts that rapid decrease in the viscosity ratio, \( \eta_c/\eta_0 \), in the central portion as the power law decreases. The statistical fit of the data to the Bingham function gives a correlation coefficient of 0.9505 and R².

Table 3. Data relating cluster size to power-law and viscosity ratio \( \eta_c/\eta_0 \).

<table>
<thead>
<tr>
<th>( Rc/R ) core fraction</th>
<th>Power-law ( n ) Model equation 5</th>
<th>( \eta_c/\eta_0 ) Newtonian model equation 14</th>
<th>( \eta_c/\eta_0 ) Bingham model equation 17</th>
<th>Prefactor - Squared model equation 19</th>
<th>Prefactor – Cubed model equation 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>0.01</td>
<td>0.011</td>
<td>0.017</td>
<td>0.034</td>
<td>0.062</td>
<td>0.103</td>
</tr>
<tr>
<td>0.10</td>
<td>0.099</td>
<td>0.104</td>
<td>0.113</td>
<td>0.116</td>
<td>0.131</td>
</tr>
<tr>
<td>0.15</td>
<td>0.099</td>
<td>0.103</td>
<td>0.113</td>
<td>0.115</td>
<td>0.126</td>
</tr>
<tr>
<td>0.20</td>
<td>0.094</td>
<td>0.097</td>
<td>0.101</td>
<td>0.106</td>
<td>0.111</td>
</tr>
<tr>
<td>0.25</td>
<td>0.092</td>
<td>0.090</td>
<td>0.099</td>
<td>0.103</td>
<td>0.108</td>
</tr>
<tr>
<td>0.30</td>
<td>0.088</td>
<td>0.082</td>
<td>0.089</td>
<td>0.095</td>
<td>0.100</td>
</tr>
<tr>
<td>0.35</td>
<td>0.084</td>
<td>0.077</td>
<td>0.083</td>
<td>0.089</td>
<td>0.095</td>
</tr>
<tr>
<td>0.40</td>
<td>0.079</td>
<td>0.070</td>
<td>0.076</td>
<td>0.082</td>
<td>0.088</td>
</tr>
<tr>
<td>0.45</td>
<td>0.074</td>
<td>0.064</td>
<td>0.069</td>
<td>0.075</td>
<td>0.081</td>
</tr>
<tr>
<td>0.50</td>
<td>0.069</td>
<td>0.058</td>
<td>0.063</td>
<td>0.069</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Figure 8. Literature data relating viscosity ratio to power-law.
value of 0.9034. The Bingham based model appears to have incorporated the essence of the relationship between the viscosity ratio and the power-law and statistically gave a reasonable fit for a purely theoretical model based on simplifying assumptions stated above.

\[
\frac{\eta_c}{\eta_0} = (1 - \varepsilon)^3 \left(1 - \frac{8}{3} \varepsilon + 2\varepsilon^2 - \frac{1}{3} \varepsilon^3 \right) \tag{19}
\]

\[
\frac{\eta_c}{\eta_0} = (1 - \varepsilon)^3 \left(1 - \frac{8}{3} \varepsilon + 2\varepsilon^2 - \frac{1}{3} \varepsilon^3 \right) \tag{20}
\]

However, the model would be more potentially useful, practically for scientific or engineering predictions, if the model represented the data scattered on both sides of the function. It was decided to determine if a simple Edisonian modification of equation 17 would provide a better fit over the entire data set while maintaining the equation functional form developed by using the percolation non-dissipating cluster based theory above. Thus, the Bingham model was modified as follows, the term that converts the Newtonian function to the Bingham function was squared and cubed, equations 19 and 20:

The data from Figure 8 were then again replotted, per Figure 10, and correlating functions using the modified Bingham function equations 19 and 20 (see table 2 columns 5 and 6) were added to the plot. It is observed that both equation 19 and 20 provide a “better/good” fit over the entire power-law range. Equation 20 gives a correlation coefficient of 0.9574 and R^2 value of 0.9166. This is an improved statistical fit compared to the Bingham model.

Polymer Observations

It is observed that the correlation for the effective filler concentration for the PS melts [53,54] was determined from the Newtonian fluid base slurry vs. filler concentration power law relationship found for PMMA beads suspended in a Newtonian fluid. This is an unexpectedly good correlation. The same analysis was carried out for the four PE neat resins used in an extended investigation [55]. The combined results for all 8 of the polymers are found in Figure 11.
The data from the entire polymer sets fall on the percolation prediction as a function of “filler concentration”. For each polymer the “effective concentration” was determined using a plot power law vs. filler concentration relating the power law and filler concentration using a Newtonian fluid filled with rigid filler.

**Implication to Extrusion Processing**

The change in power law as a function of filler content or polymer molecular weight has a strong implication on the ability to increase productivity by increasing the throughput in an extrusion die or an injection mold.

There is a very non-linear relationship between the onset of the second Newtonian plateau and the power law, Figure 10 for Newtonian fluid based slurries. When the second Newtonian plateau is reached, the power needed to increase the velocity through the die or mold runners goes up linearly with flow rate because shear stress and shear rate are again linearly linked. When investigating and evaluating a “capillary Rheometer” at General Motors Research in the 1970s, we put a capillary die on the end of the injection unit of a injection molding machine. Two resin responses were typical, a polystyrene with a power law of about 0.6 and a PP with a power law of about .06. The maximum shear rate we could achieve for the PS was about 50,000 s⁻¹, while for the PP we reached the apparent second Newtonian plateau at about 200,000 s⁻¹. The second Newtonian plateau was indicated by the observation that setting the injection speed control to a higher value essentially resulted in no increase in injection rate.

As the power law decreases toward 0.0 the transition to the Infinite Newtonian plateau occurs at a lower apparent viscosity and at a higher shear rate, Figure. It needs to be remembered though that the lower apparent viscosity is associated with a higher shear stress because of the manner that we analyze shear thinning viscous characteristics.

**Figure 11.** Percolation correlation for the power law for both PS and PE polymer melts.

**Figure 12.** Effect of power law on transition to second Newtonian Plateau.

4. **Summary**

This paper has related the three rheological zones illustrated in Figure 1, η, the shear viscosity, the power-law n, and the η/η₀ viscosity ratio to percolation theory based functions. The analysis would be valid when the filler concentration in the slurry is equal to or exceeds the percolation concentration, when it is expected that there will be macroscopic clusters in the system. The theoretical zero shear and the power-law functions fit the data very well. Figures 5 and 6 demonstrated that the power-law, proposed here to represent the fraction of the fluid dissipating energy, is a function of the size of the non-deforming clusters in highly filled slurries that can be quantified in tube flow as the size of the central core of the flowing slurry. The η/η₀ data presented here suggest that this ratio is also a function of the volume of non-dissipating clusters as that value fixes the fraction of the slurry that can dissipate energy. The η/η₀ viscosity function from the Bingham theory shows the correct trends and has a reasonable statistical fit to the data. However, this function needs to be modified to produce a fit for this broad range of literature data that has data scattered on both sides of the function. Further, it has been demonstrated that the power-law, equation 5, with equation 20, can be used to predict the value of the viscosity ratio, η/η₀, for this broad range of materials and shear fields. Although, the Bingham theoretical function
appears to have the correct form, more work needs to be
done to make it theoretically more quantitative. Finally,
since a minor change in the theory produces an excellent
fit, it suggests that the form of the equation, equation 17,
may be correct.

5. References

15. F. Gadala-Maria and A. Acrivos, (1980) J. Rheol., 24 (6), 799,
30. R. Simha, (1952) J. App. Phys., 23 (9), 1020,
34. G. K. Batchelor, (1977)J. Fluid Mech., 83 (1), 97,
38. V. Vand, (1948)J. Phys. Coll. Chem., 52, 277,