Correlation between filler concentration and viscosity power-law for polymer slurries

Gregory A. Campbell and Mark D. Wetzel

A new predictive relationship that is based on percolation theory concepts has been verified with tubular flow experiments.

Polymer slurries with high filler contents (e.g., the starting materials for sheet-molding compounds and polymer-based inks) can present a variety of processing challenges, including high screw-shaft torque, energy consumption, pressure, and temperatures. In addition, these slurries exhibit shear thinning behavior under deformation conditions (e.g., when they are used in extrusion systems). At very low shear rates, the viscosity of slurries acts in a Newtonian manner (see Figure 1). With increasing shear rate, however, the apparent viscosity tends to decrease and eventually becomes Newtonian again at high shear rates (at a lower 'infinite' shear viscosity). In the case of simple, one-velocity component flow the viscosity-power-law relationship is:

$$\eta = k \, |\dot{\gamma}|^{n-1} \tag{1}$$

where η is the viscosity, $\dot{\gamma}$ is the one-component shear rate (viscosity is positive definite), and n is the power-law constant. Although there has been much research on the rheology of highly filled polymers,[1–3] there has not yet been a focus on the effects of filler concentration on melt processing.

In many previous studies,[4–24] it has been shown that macroscopic structures are created in highly filled slurries when the suspension is deformed, and that these macroscopic clusters of agglomerated particles have a significant effect on the deformation behavior of the suspension. Furthermore, experimental evidence[6, 7, 10, 12, 18] shows that there is no motion of the particles within these clusters. These observations led to the hypothesis that the power-law constant, n, of the viscosity curve represents the change in volumetric energy dissipation, which is related to cluster formation (a function of filler concentration and shear rate).[4, 5] It has also previously been proposed[25] that, at low shear rates, particles in a cluster have time to rearrange and thus allow the cluster to deform (i.e., as a result of the imposed flow field). This gives rise to a Newtonian viscosity and is similar to the concept of a characteristic
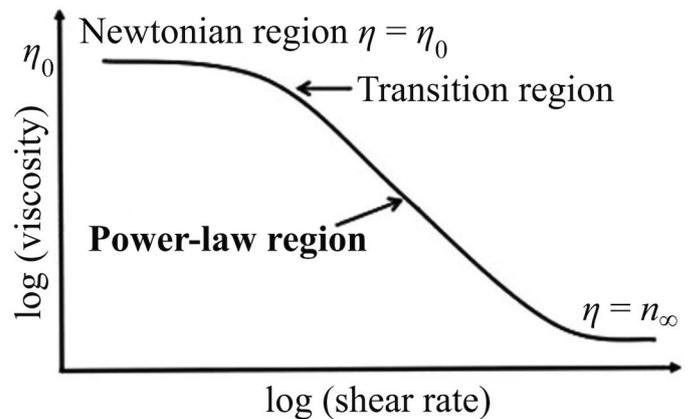

***Figure 1.** The viscosity (η) of polymer suspensions as a function of shear rate. At very low shear rates the viscosity of slurries acts in a Newtonian manner. As the shear rate increases, the viscosity decreases until it becomes Newtonian again at the highest shear rates. The viscosity of the slurry is equal to the zero-shear viscosity (η_0) and an infinite-shear viscosity (η_∞) in the low and high shear-rate Newtonian regions, respectively. In the power-law region, the viscosity is described by the relationship in Equation 1.*

time for a material[26] (i.e., the time required for a significant local structural change to occur in an unsheared material). In earlier work, this percolation-based theory has been used to investigate poly(methyl methacrylate), PMMA, slurries.[4, 5]

In our work we have developed an analytical tool that can be used to predict the flow characteristics of highly filled slurries that have a Newtonian continuous phase, but that also exhibit shear thinning or power-law characteristics. We have thus found a new non-linear function that correlates n to the concentration of the filler in the slurry. The behavior of this function suggests that the Newtonian-to-power-law transition is dominated by percolation processes.

We investigated the capillary flow of calcium-carbonate-filled slurries, which allowed us to formulate a percolation-theory-based function that correlates all of the data in the power-law region. To extend our fundamental understanding, we chose PMMA beads as the filler material in subsequent experiments. For these tests, we developed our own experimental setup. We used a PMMA capillary to measure the flow characteristics of the PMMA slurry. We also used a differential pressure transducer and thus measured the pressure drop across the capillary tube as the slurry was tested (i.e., a classical approach for

Figure 4. The power-law-concentration relationship for poly(methyl methacrylate)—PMMA—slurries. Lines indicate percolation model predictions in comparison to experimentally obtained data (squares and circles) from two different studies (i.e., 'Zak'[4] and 'JP'[5]). Different values for the percolation concentration (ϕ_c) and the maximum packing concentration (ϕ_m) were used in the two approaches. ϕ: Filler concentration.
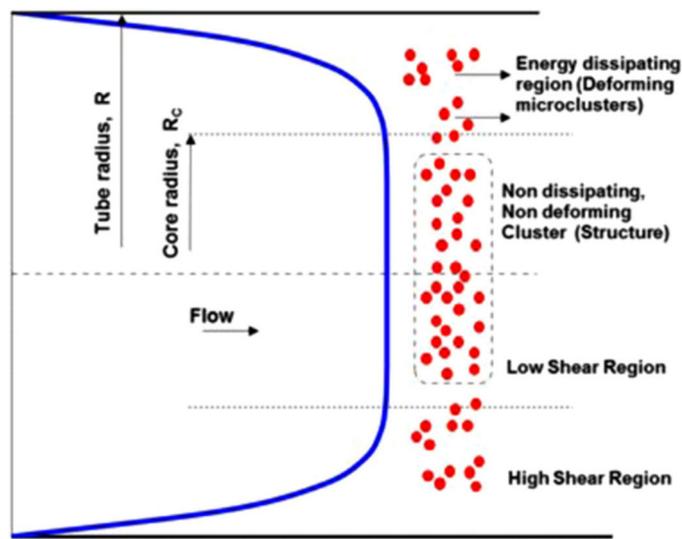
Figure 2. Slurry velocity profile that illustrates (schematically) the formation of deformable and non-deformable cluster structures in the tube during capillary geometry measurements.
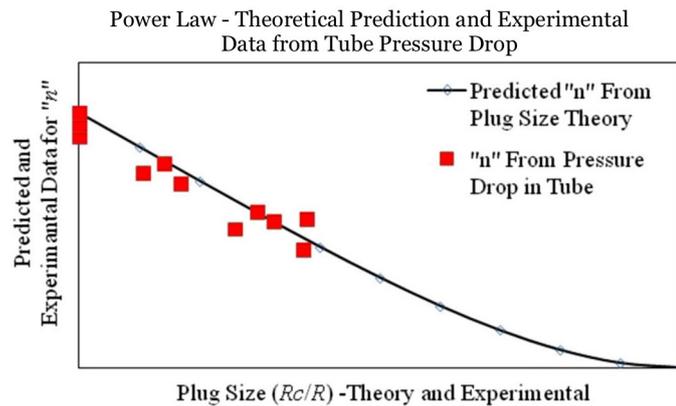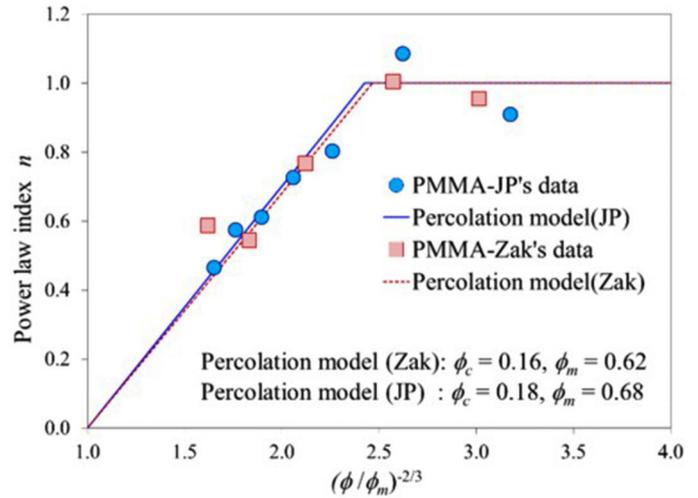
Figure 3. The theoretically predicted power-law (n) as a function of core radius/tube radius (Rc/R) ratio (black line). Experimental results (red squares) fit the predicted n extremely well.

evaluating n).[27] In addition, we obtained videos during the experiments so that we could determine the local velocity in the tube, as a function of position across the tube, and to evaluate the average fluid flow rate. A schematic illustration of the measured flow characteristics is shown in Figure 2.

Literature results from previous experiments[7, 8] provided information concerning the shape of the slurry velocity profile, as well as the size and location, of non-dissipative structures (i.e., core clusters) during Poiseuille flow. Similar information was also obtained in a nuclear magnetic resonance imaging study.[28] Based on the results of our experiments (described in the previous paragraph), we chose to use a Bingham model of the stress tensor to model the flow behavior (i.e., assuming that the local stress is Newtonian above a critical shear stress level[25]) in the dissipative region of the flow field in our slurries. Using our new theoretical function for n,[27, 29] we can thus predict n as a function of the core radius/tube radius ratio. We find that our experimental data[4, 5] follow our new theoretical prediction extremely well (see Figure 3).[27, 29] These results strongly suggest that the development of non-dissipative clusters is the main cause of shear thinning in the slurries we have examined. The same predictive theory—used to correlate the calcium carbonate data—has also been used[4, 5] to correlate n
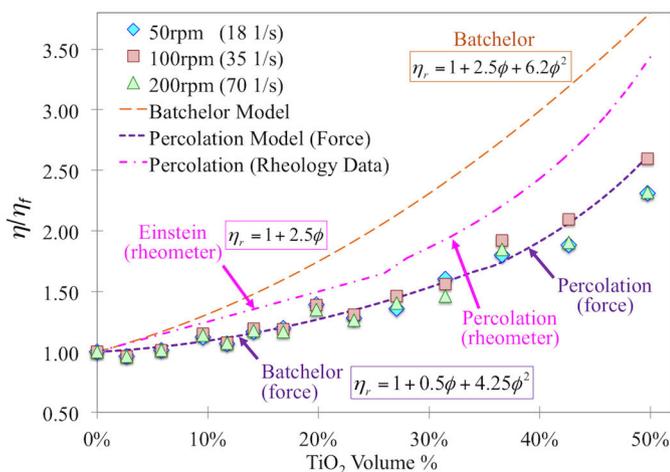
Figure 5. Relative viscosity data for concentrated titanium dioxide (TiO$_2$), low-density polyethylene slurries, expressed as a function of TiO$_2$ concentration. Experimental results (data points) were obtained from melt-blending experiments on a conical twin-screw batch mixer. Three different model curves (dashed lines) are shown for comparison. η and η_f: Viscosity of fluid with and without filler, respectively.

for the PMMA slurries in the percolation concentration (ϕ_c) range (see Figure 4). Different criteria were used to determine the maximum packing concentration (ϕ_m and ϕ_c) constants, but both approaches provide an excellent correlation with the experimental data obtained in each study. Moreover, the results indicate that n deviates from 1 at about 17% filler concentration.

In another part of our work we conducted melt-blending experiments on concentrated titanium dioxide (TiO$_2$), low-density polyethylene slurries to evaluate their processability.[30] For these experiments we used a 15cc conical twin-screw batch mixer (from Xplore Instruments BV, The Netherlands). The relative viscosity data—estimated from barrel force measurements—are plotted in Figure 5 as a function of TiO$_2$ loading. These experimental results are shown in comparison with several constitutive model curves. We find that the classical Batchelor model overestimates the viscosity increase observed in the experimental data. The Campbell-Forgacs model[25] (i.e., based on capillary rheology data) also predicts relative viscosities that are higher than those estimated from the force data (the percolation model). By making adjustments to our model parameters, we can obtain a better overall fit for all TiO$_2$ concentrations.

In summary, we have developed a new predictive viscosity power-law relationship for polymer slurries with high filler concentrations. Our relationship is based on percolation theory concepts and provides a correlation between the power-law constant and the concentration of the filler within the slurry. We have also conducted a series of rheological experiments to verify the accuracy of our theoretical predictions.

We expect to extend this work by investigating the interactions among filler particle size, filler concentration, and polymer molecular weight, and how these parameters influence the flow characteristics of a family of polyethylenes.

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Gregory Campbell is an emeritus professor who was on the faculty of Clarkson University for 24 years, beginning in 1984. He served as chair of the Chemical Engineering Department, the university's chief information officer, and the dean of engineering. He also worked for 13 years at General Motors Research Laboratory and at Mobil Chemical Research for three years. During his time at Clarkson University he supervised more than 25 advanced degree students. He has been active in the Extrusion Division of SPE, has more than 80 publications, and he recently co-authored a book (*Analyzing and Troubleshooting Single-Screw Extruders*). He has consulted in the areas of polyurethanes, film processes, extrusion, and slurry dynamics.

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