CASE STUDY

Insights into Yield Stress Effects During Dispense: A CFD Analysis of DOWSIL™ 7091 Adhesive Sealant and Other Thixotropic Sealants

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DOWSIL™ 7091 Sealant is an alkoxy-cure, silicone sealant used as a formed-in-place gasket (FIPG) material in a wide variety of automotive applications and renowned for its adhesion performance over a wide variety of substrates including enameled and painted steel, aluminum, ceramic and glass as well as to certain plastics used in engineering applications. It is used in applications which demand a strong but flexible bond, such as when bonding materials with differing thermal expansion rates, e.g. glass to metal or glass to plastic.

Fluids that contain fillers, such as fumed silica, often exhibit complex rheological behavior with an apparent yield stress due to the networks that are formed by the filler. These so-called Yield-Stress Fluids (YSF) behave like an elastic solid when subjected to stresses below some critical value and transition to liquid-like behavior above this “yield stress”. The yield stress to start the flow from a static condition is often higher than the yield stress to maintain flow, resulting in a pumping pressure overshoot when initiating flow in a pipe. If the pump pressure (stress) is slowly increased, the solid like material may deform elastically and then begin moving as a solid plug due to slip at the wall (this slip condition has been associated with a lubrication effect due to a lower filler concentration in a thin layer near the wall). The critical wall stress to induce slip is less than the yield stress and depends on the fluid-wall interactions, which are in turn impacted by wall roughness. As the applied pressure continues to increase, the stresses near the wall region will reach the yield stress first allowing the material near the wall to begin to flow like a fluid, while the material near the lower stress center is carried along in a solid-like plug flow. This YSF behavior has implications concerning the impact of the applied pressure profile on the flowrate and resulting extrudate pattern during start-up or transition of flow through a hose leading to an applicator nozzle. This effect becomes larger as the volume concentration of solid particles increases[1].

Silicone sealants and adhesives, being filled elastomeric materials, can exhibit a wide range of complex rheological properties including thixotropy, high yield stress as discussed in the previous paragraph, shear thinning, viscoelastic behavior, and compressibility in some instances. These different behaviors are often inherent and are tuned in these materials to enable them to perform as needed in the application.

DOWSIL™ 7091 Sealant, being a filled silicone elastomer, exhibits a shear thinning behavior, has a high yield stress and could exhibit compressible behavior in its uncured state. Other silicone elastomers exhibit similar behavior, especially those which are highly filled. To better understand which of these material properties were significantly contributing to the dispensing issue observed by Graco where flow rate could not be consistently controlled upon initial dispensing, an evaluation of both the compressibility and the effect of yield stress was performed. Pressure Volume Temperature (PVT) testing was conducted on the uncured material to quantify its level of compressibility and Computational Fluid Dynamics (CFD) Modeling was conducted to understand the yield stress affects which would be observed under various conditions.

The PVT analysis of DOWSIL™ 7091 Sealant revealed that, while compressible, the effect observed during the dispensing of the material using Graco dispensing equipment was not primarily due to compression of the material upon startup, as had been hypothesized. This conclusion is based on the specific volume data gathered as a function of pressure at various isothermal conditions (30°C, 40°C and 50°C), which should be representative of the typical temperatures which may be seen during dispensing. These results are seen in **Figure 1**.

Footer [1]: Texas Instruments, Understanding Rheology of Structured Fluids AAN016, (2023), Internet PDF pp. 1-5.

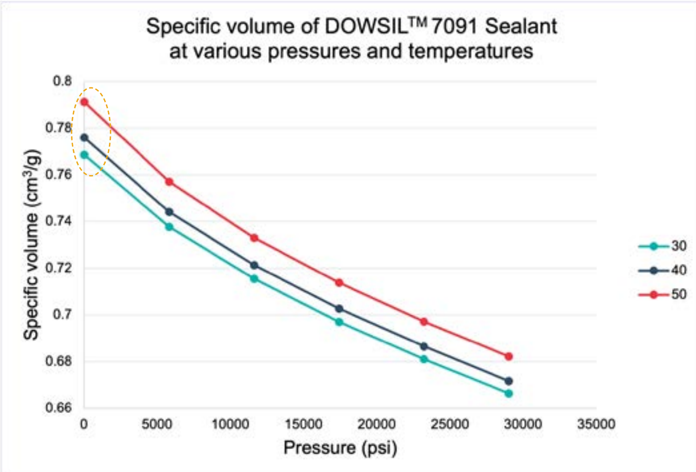

Figure 1: Specific volume of DOWSIL™ 7091 Sealant over a pressure sweep at various temperatures.

Since the pressure gradient within the equipment is an inlet pressure of ~1400 psi and an outlet pressure of 200 psi, the regime of compressibility we are interested in is at the very low end of the sweep. This indicates minimal compressibility of the sealant at those pressures or over that 1200 psi gradient. Assuming a direct correlation of specific volume to flow rate, one would expect a decrease in flow of ~1.3% at 1400 vs. 200 psi. This would not account for the large surge in flow that is seen at the outlet after the material returns to atmospheric pressure. For this reason, Dow does not believe compressibility of DOWSIL™ 7091 is the root cause of this issue.

When considering the yield stress behavior of a high solids content material such as in DOWSIL™ 7091, we again note that the material will behave like a solid until the stress (related to pressure) in the region is high enough for the material to yield and begin to flow as a fluid. This effect can negatively impact dispensability especially if there is variable pressure such as when the flow is initiated or during cycling of the pump pressure. The material will remain unyielded (no flow) until the pressure is high enough to exceed the yield stress. When the material does yield, there can be a rapid increase in flowrate. The material flow rate can be difficult to control without accounting for this yield stress effect.

It should be noted that if the material were highly compressible, a similar phenomenon could be observed as the initial pressure increase would go into compressing the material rather than moving it forward, which is why this evaluation was performed. Furthermore, if the material was both compressible and had a yield stress, the effects could be compounded as the higher pressure needed to overcome the yield stress would also compress the material. Then, when it reaches the low-pressure outlet of the dispense equipment, it can expand, again resulting in poor controllability of the dispense rate.

In order to gain understanding of the yield stress effect on flow profiles in a representative pipe, CFD simulations were run at two different steady state flowrates: 0.252 kg/hr to represent start-up and 2.52 kg/hr to represent normal operation.

A Hershel-Bulkley rheology model was used to capture the yield stress behavior:

$$\mu = min\left(\mu_0, \frac{\tau_0}{\dot{\gamma}} + k\dot{\gamma}^{n-1}\right)$$

Where μ is the effective viscosity, $\dot{\gamma}$ is the shear rate, τ_0 is the yield stress, k and n are the shear thinning parameters, and μ_o is a plateau viscosity at low shear rates chosen to be an arbitrary high value to create a solid-like state.

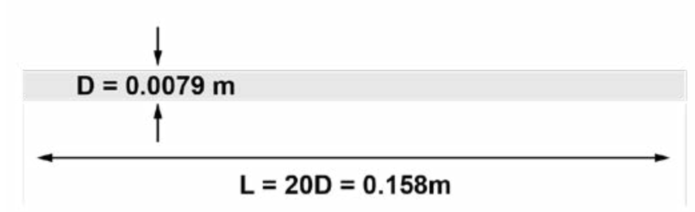

Figure 2: Diameter and length of pipe used for CFD modeling of DOWSIL™ 7091.

The modeling domain was as shown in **Figure 2**:

20D was chosen as the length of the pipe which is adequate for the steady state model as the entry length is << 1D and flow profile will not significantly change at longer lengths. Other assumptions include:

- No-slip wall boundary conditions (possible wall slip behavior not considered)
- Density: 1400 kg/m^3
- Hershel-Bulkley model parameters for DOWSIL™ 7091:
    - τ_0 = 445.32 Pa
    - k = 235 Pa-s^n
    - n = 0.77
    - μ_o = 3000 Pa-s

The resulting viscosity as a function of shear rate is shown in **Figure 3**.

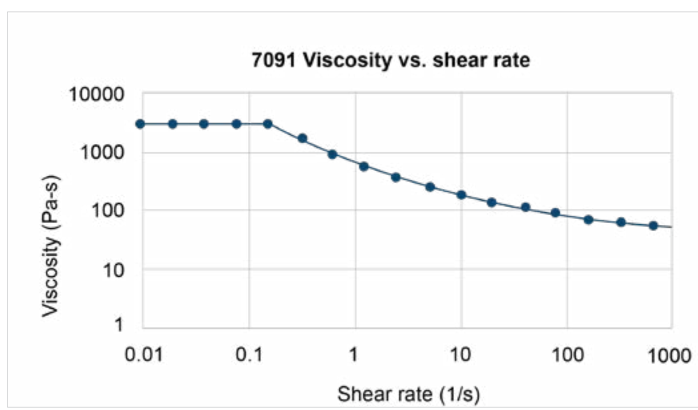

Figure 3: Viscosity of DOWSIL™ 7091 Sealant as a Function of Shear Rate

The CFD analysis indicated that significant differences to the flow profile would be observed at start-up vs. at standard operating conditions as shown in **Figure 4** and **Figure 5** respectively, where the black regions indicate the unyielded solid-like core and the tan regions represent the yielded fluid-like region. This is also seen in the velocity vectors which indicate a parabolic type of flow profile near the walls and a plug flow in the center.

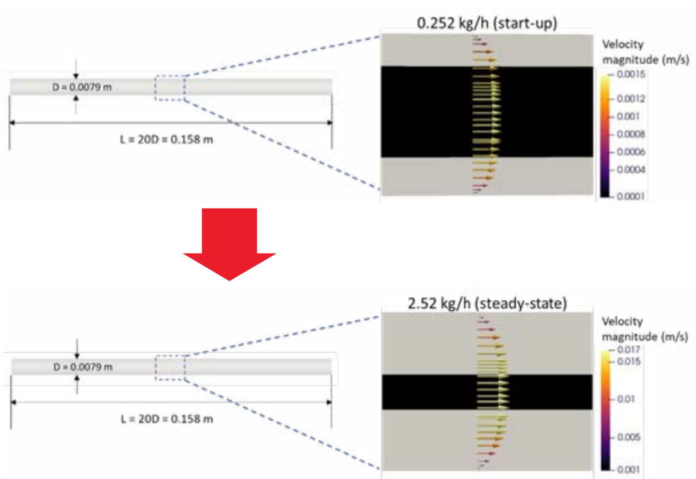

Figure 4: Predicted velocity of fluid in pipe at low flow (start-up) conditions.
Figure 5: Predicted velocity of fluid in pipe at normal operating conditions.

This model predicted a pressure drop of 1064 psi at 2.52 kg/hr, which can be compared to the measured pressure drop of 1200 psi, indicating good fit of the model with the empirical data. As the figures suggest, at lower flow rates, only the material close to the wall is behaving like a fluid. Most of the material is in the solid-like core. At higher flow rates, a larger portion of the material is behaving like a fluid, with a small unyielded core.

The effect of yield stress on pressure drop was also investigated by running an additional simulation at the higher flow rate, but with a higher yield stress as well. **Figure 6** shows the upward shift in the viscosity vs. shear rate curve with a yield stress of τ_0 = 2000 Pa. **Figure 7** shows the flow profile comparison for the original yield stress of τ_0 = 445.32 Pa and the new yield stress of τ_0 = 2000 Pa. It is observed that the higher yield stress results in a wider unyielded core region.

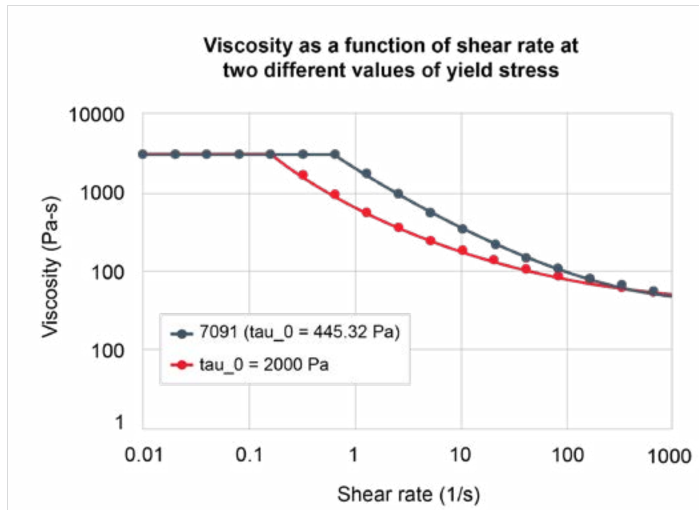

Figure 6: Viscosity as a function of shear rate at two different values of yield stress.

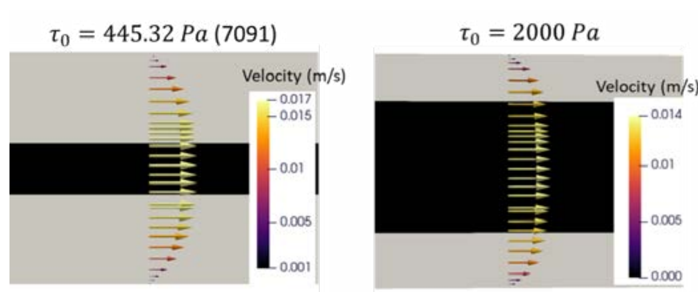

Figure 7: Flow behavior of a higher yield stress fluid VS. DOWSIL™ 7091 at same flow rate (2.52 kg/hr) and pipe dimensions.

Table 1 summarizes a number of simulation results from the three cases described above. As has already been observed, the unyielded core region is larger with both a lower flow rate and with a higher yield stress. Pressure drop decreases with decreasing flow rate (0.39X pressure drop decrease with 0.1X flow rate), but the relative decrease is significantly less than would be expected for a Newtonian fluid (where the pressure drop will decrease linearly with flow rate). This is primarily due to the shear thinning nature of the material in the yielded state (2.8X viscosity increase with 0.1X flow rate), but is also impacted by the narrower yielded region which results in a higher velocity gradient (strain rate) near the wall when comparing with a Newtonian fluid at a same flow rate. The pressure drop increases with increasing yield stress, which correlates to a larger unyielded core and can be related to the increase in both strain rate (1.32X) and viscosity (1.47X) near the wall; i.e., 1.93X pressure drop = 1.47X viscosity * 1.32X strain rate.

Flow rate (kg/hr)	Yield stress τ_0 (Pa)	k	n	Unyield core width / pipe diameter (m)	Pressure drop (psi)	Viscosity at wall (Pa-s)	Strain rate at wall (1/s)	Wall shear stress = wall viscosity *strain (shear) rate at wall (Pa)
2.52	445.32	235	0.77	00.22	1064	168	12.3	2069.8
0.252	445.32	235	0.77	0.56	411	471	1.7	798.9
2.52	2000	235	0.77	0.51	2057	246.4	16.2	4000.9

Table 1: Simulation predictions of for different flow rates and yield stress value.

Conclusion

The quick CFD analysis of the steady state flow of a yield stress fluid in a pipe provides insights into the presence of an unyielded core region and the impact of this core on the wall strain rate, viscosity, and resulting pressure drop. It does not fully capture the start-up effects or effects of flow through the contracted nozzle. That said, given the low compressibility observed in DOWSIL™ 7091 Adhesive Sealant and other thixotropic sealants and adhesives which often exhibit similar complex rheological behavior when dispensing, these initial findings are sufficient to conclude yield stress effects are the primary cause of the effect studied.

This known challenge in dispensing at start-up has been addressed by Graco through a software upgrade which manages the initial variability in flow rate that is observed.

Literature

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