Effects of Molecular Homogenization
Three-Dimensional Mixing

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1974 -1987 Killion Extruders:

- Sale Manager 1974-1976
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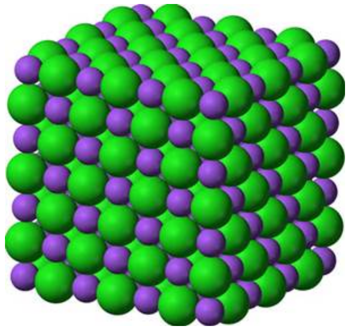
1988 to Present: Founder/President of Randcastle Extrusion Systems—a manufacturer of small extrusion equipment. Six patents on extrusion including compounding, pressure stability and coextrusion with an additional patent pending for compounding (the topic of papers being delivered for this conference).

Speaker Photo:

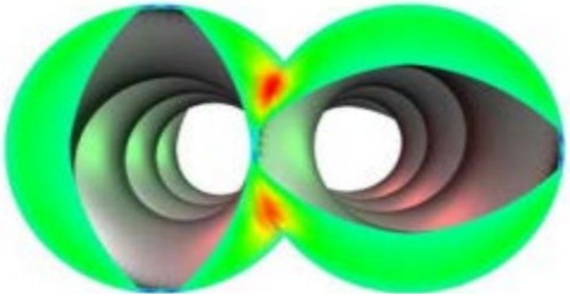
INTRODUCTION

The goal of mixing, the mixture to strive for, is best emulated in a three-dimensional crystal composed of two different size atoms. Nothing is mixed better. Nothing you can do to this crystal improves the mix.



Only a mixer organizes atom by atom can create such a mix. Likewise, we can judge a polymer mixer by its orderliness. Every step in the mixing process must organize the mixture in a step-by-step fashion. A mixer that functions in a disorderly manner, that mixes some here, some there, a little better over there, not at all in this part, cannot consistently produce an orderly product.

The corotating twin screw extruder (CRST) is well known for its dispersive mixing ability. It is generally deemed the most flexible dispersive (to break ups) mixer and a good distributive mixer. However, it is not an orderly, organizing mixer. It's distribution of ingredients is flawed by its mixing method:



In the cross section of a corotating twin, above, there is only a small amount of elongation at the kneading block intersection where stretching—and elongational mixing—takes place. It is not an ordering mixer so, ultimately, it cannot produce an orderly product. It is well understood that most of the material will flow past the intersection without elongation. While there are often many intersections, a small percentage at every one can never mix 100% of the mass. Some amount is not elongated and so not mixed at all. While most of this paper discusses small molecules such as water vapor, oil, and gases, the lack of mixing also matters to larger scale mixtures such as particulate and gels.

Say that 4% of some error (dirt, a cluster of gels or a group of fine bubbles) is undistributed in a tensile bar that is otherwise perfect. Failure will occur starting at the agglomeration. For such very fine errors, every tensile bar will likely have such an error and will fail starting at the error. But, if such fine errors were well distributed, failure would then occur at a higher load. All the tensile bars would be stronger. Many of our physical tests are similar. An ordering distributive mixer can improve the physical properties because it mixes all the mass in an organized, repeated method.

At the scale of small molecules such as water vapor, it is important to differentiate the CRTS, single screw mixers, conical twins, counter rotating twins, etc. Such mixers are not described as organizing three-dimensional mixers. That is, they do not suggest that:

- The X axis of mixing is first mixed by this mechanism.
- The Y axis of mixing is then mixed this way.
- The Z axis of mixing is mixed by this method.
- The X, Y, Z mixing above is then repeated as often as necessary to reach the goal.

That is how a distributive mixer should be described.

Further, a three-dimensional mixer should be capable of variation for the type of feed and use:

- **Solids Feed Single Screw Extruders:**
    - **Lab Extruders:** Pellets, granulations and powders are known to feed in the Molecular Homogenizer. Because of the low shear of small screws, the initial mixers are adapted to increase melting through elongation and subsequent mixers for fine distribution, sequestering water vapor and degassing.
    - **Production Extruders:** Barrier screws are well-known to melt at high production rates. It may be possible to replace existing mixers on such screws with the Molecular Homogenizer for improved distributive mixing.

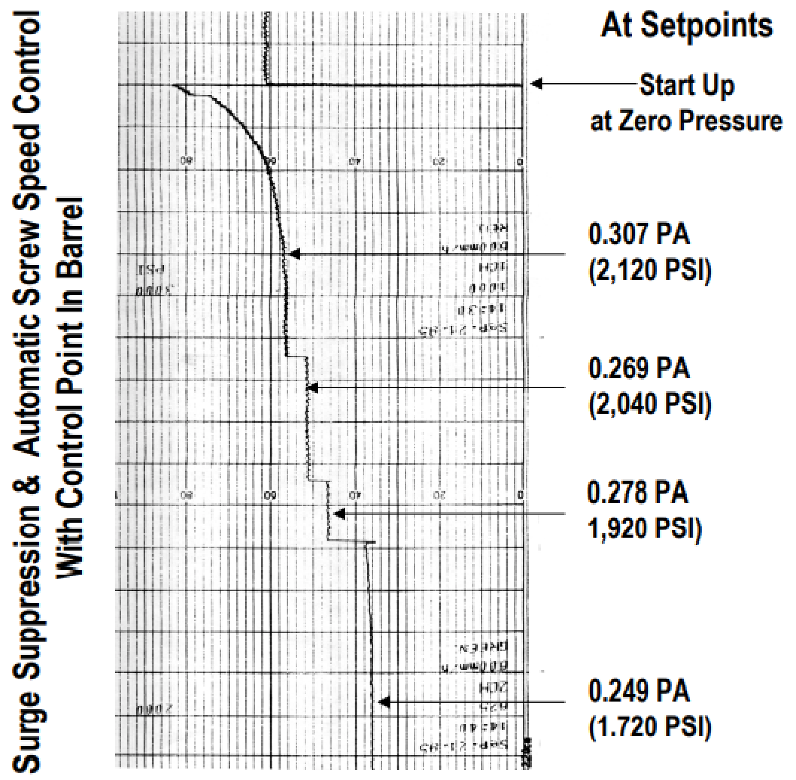
- **Melt Input:**
    - **Twin Screws:** Twins, such as the CRTS, have a long and varied history as extremely useful tools for dispersive mixers and for coarse distribution. The melt from a twin can then be fed into the Molecular Homogenizer. Then, the Molecular Homogenizer can add fine distribution, water vapor sequestering or fine gas removal prior to the downstream takeoff. An additional advantage is that the Molecular Homognizer can generate gear pump like pressures for “direct extrusion” without the complexity of a gear pump. The Molecular Homogenizer does not have the need for a complex control algorithm to alter feeding and screw speed ahead of the gear pump; the typical pressure variation produced by the twin a sufficient for the input of the Molecular Homogenizer.

- **Polymer Reactors:**
  - **Production Polymer Reactors:** At the end of a polymer reactor is a single or twin screw extruder that feeds a pelletizer that discharges pellets. Both create a pressurized polymer stream where the polymer is dry. The Molecular Homogenizer can remove:
    - **Gases:** Some extruders are known to insufficiently degas residual monomer. The Molecular Homogenizer's very large surface area, the thin film created during extension and repeated mixing exposes the gas for removal.
    - **Water Vapor Exclusion:** Experiments to date have shown that dried hygroscopic materials, that normally absorb water vapor in 4 to 6 hours can be extended to more than three days. Work is under way to extend the time to at least months. If successful, normally hygroscopic materials would not have to dried when efficiently consumed. The energy and handling benefits are obvious.
  - **Small Lab Reactors:** Some lab reactors discharge the melt by gravity into a shaped feed section. The Molecular Homogenizer can be fitted with such a shaped feed. The Molecular Homogenizer's very large surface area, the thin film created during extension and repeated mixing exposes the gas for removal.

THE MOLECULAR HOMOGENIZER

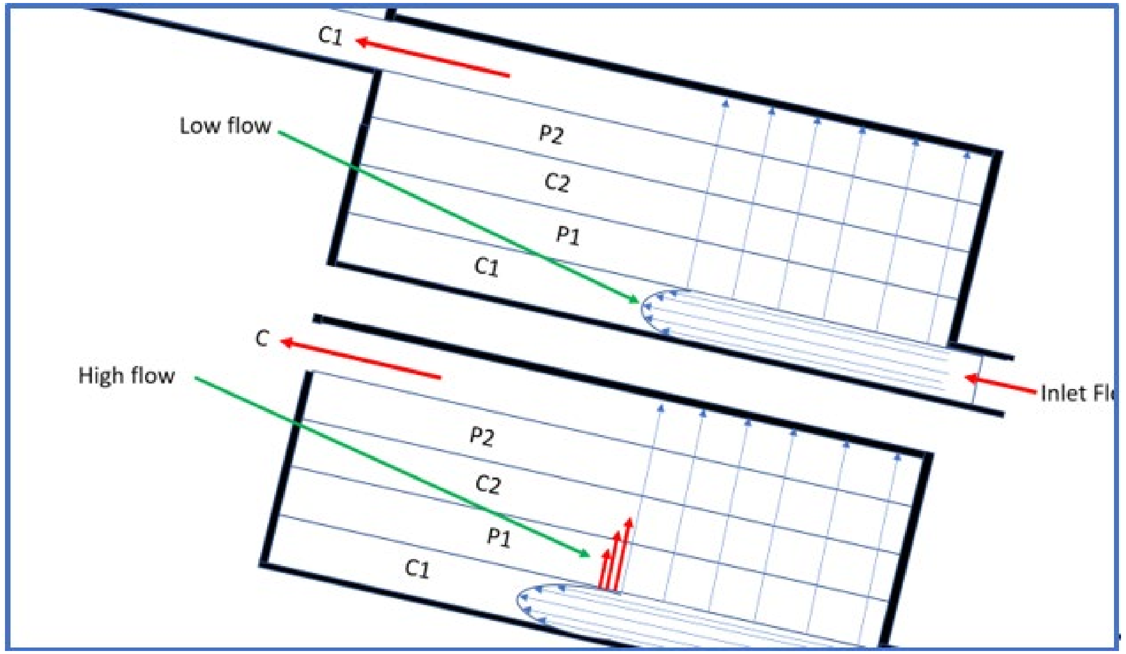
Pressure Stability

One of the key properties of the Molecular Homogenizer is its pressure stability. This is somewhat surprising for a starve fed extruder. Accumulators are well known to dampen variable flow. That is, they can lessen the pressure variation. In extrusion, pressure variation is often called surging. Randcastle patented surge suppression as described at Antec (see https://static1.squarespace.com/static/5ff4cbe29ed5f916ac08eca3/t/60084cc3668aee6485250138/1611156678375/surgesup.pdf) showing that large and small accumulators (partly empty channels) were show to control surging. In one study, the pressure was controlled at the push of a button with gear pump like pressure of +- 10 psi.



The surge suppression innovations were limited by the size (very small) and number (one or two) channels. Nevertheless, the technique was sufficient to allow automatic screw speed control for plus/minus 10 psi—the same as a gear pump as shown above.

The C1 channel of the Molecular Homogenizer acts as an accumulator as shown in the drawing below:



Mass variation in the C1 channel of the mixer changes the fill length. It takes time for change in mass to arrive at the C3 channel so the pressure variation is lessened. The Molecular Homogenizer accumulators are excellent surge suppressors because:

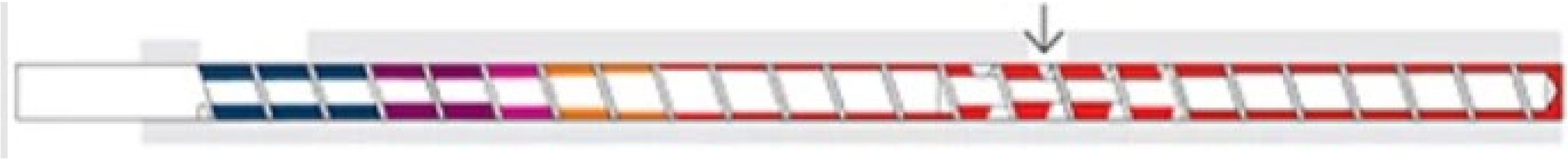
- **Large Capacity Channels:** The channels used to suppress the surges are large. This means that large surges can be reduced whereas the original invention was limited to small surges.
- **Serial Sets:** There are seven individual C1, P1, C2, P2, C3 sets in the tested Molecular Homogenizer. Each one reduces the surging of the previous one until the pressure becomes very uniform. In testing of the Molecular Homogenizer—and without adjusting the process temperatures in the tests for improvement—plus minus 30 pounds was maintained. No screens were used to help dampen the pressure variation.

Product Extrusion

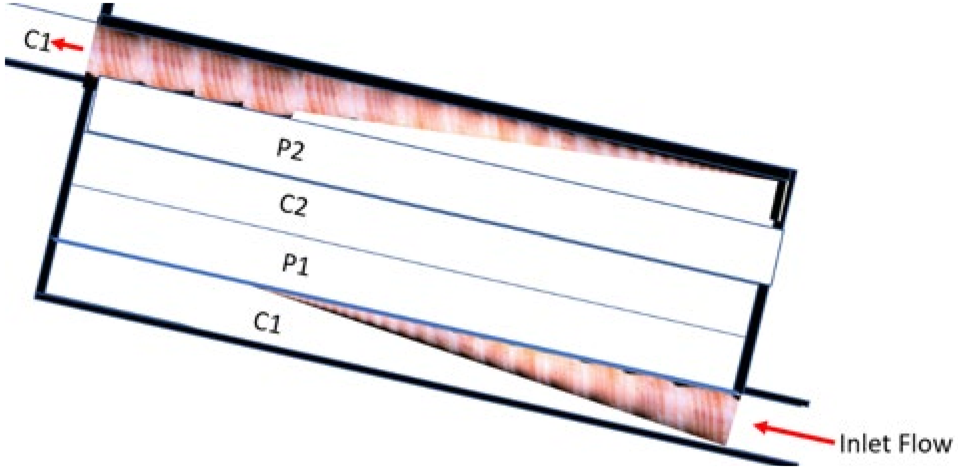
- **Single Screws:**
  - **Pressure Stable Pumps:** Single screws are well known for high pressure, pressure stable, pumping. This allows cast and blown films, tubing, pipe, sheet, etc.
  - **Gear Pumps:** Because gear pumps allow only a very fixed output per revolution, the input pressure must be controlled. The pressure must not be too great or the gears in the pump will be pushed into the surrounding walls and seize. The pressure must not be so low as to cause the pump to cavitate. This is routinely handled by automatic screw speed control. The gear pump creates very stable pressures and can allow marginal screws to function. While gear pumps are common on single screw, they are expensive and add a small degree of complexity.
  - **Molecular Homogenizer:** The Molecular Homogenizer retains its ability as a single screw to generate high, pressure stable, outputs. So, it can make cast film, blown film, etc. Adding a feeder adds some complexity and expense. However, the requirements for the Molecular Homogenizer were simple. A conveyor type volumetric feeder was used with minimal control (see, How To Create Tetherball Mixing, page 8).
  - **Twin Screws And Direct Extrusion:** Twin screws are well known for low pressure development and pressure stability only sufficient for pelletizing. "Direct extrusion" is the term used by twin screw extruders when they link a gear pump to the twin. The gear pump then builds sufficient, stable pressure to extrude a product. However, control of the gear pumps inlet pressure becomes very much more complicated than in a single screw. In a twin, mass flow is controlled by the upstream feeder. So, there is a significant time delay from the time the feeder output changes, and that material arrives at the gear pump inlet. The control algorithm that maintains the inlet pressure becomes a combination of feeder control and screw speed control. This is a complex arrangement. Changes in feedstock, as can be normal from lot to lot, can require a different algorithm.

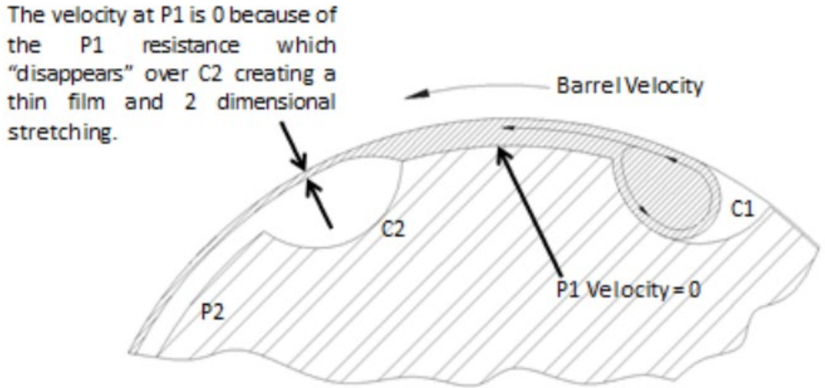
Venting

- The Molecular Homogenizer, like a twin screw, operates at zero pressure over much of its length. So, vents for extracting gas, or for gaseous input, are possible. A traditional two stage single screw uses a vent over the decompression section. The screw is empty on the trailing flight. The pushing flight is a large melted mass. Gases on the outside of the melt will readily burst and release gas. However, gases below the surface do not readily burst, are then recompressed and move forward. This is a poor venting mechanism.



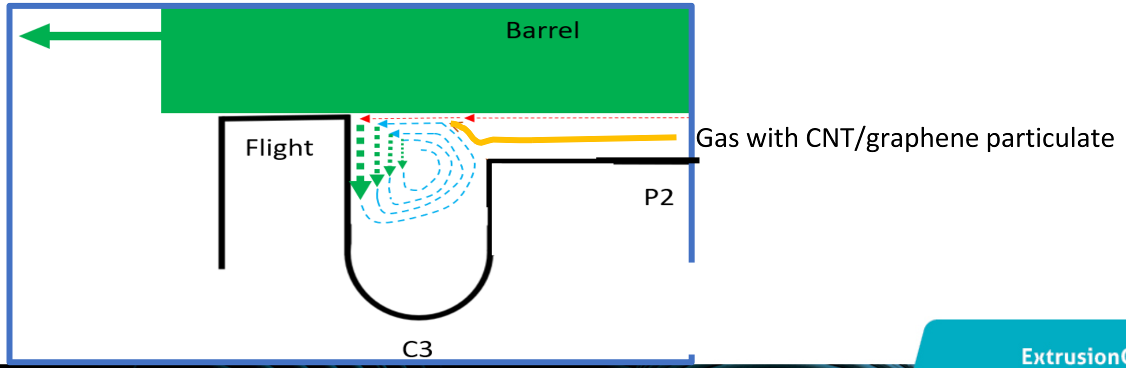
Contrast the surface area of the two-stage screw to the Molecular Homogenizer. The C1 flow constantly exposes new surface for degassing (below left). Flow over C2 (below right) is a very thin film around 0.0015 inches thick. This occurs within a single C1, P1, C2, P2, C3 mixing set. The molecular homogenizer tested had seven mixing sets.





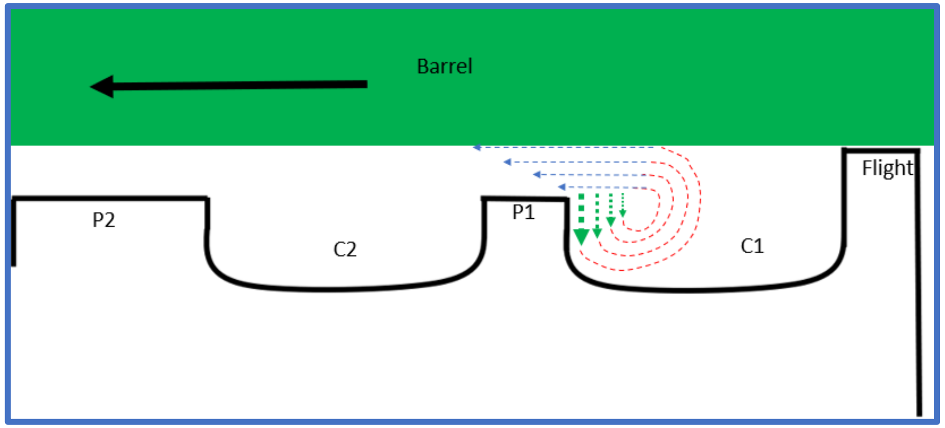
Additionally, the inner and outer flow are inverted (described in the three-dimensional mixing section). There are orders of magnitude more surface area exposed for degassing in the Molecular Homogenizer than in a two-stage screw.

The Molecular Homogenizer can be used to input gases. Multiple vents are possible in either as single C1, P1, C2, P2, C3 set or over the entire mixer. One intriguing idea to to introduce a gas carrying CNT's or graphene. Since the polymer is sticky, the particulate might be conveyed onto the large surface area and then layered into tetherball as shown below (yellow arrow):



How To Create Tetherball Mixing During Extrusion

The operating principle is to starve feed the Molecular Homogenizer screw so that the melted material is tethered to the slide of the flight. This yields a small contact area for minimal resistance and maximum spiral stretching:



The Molecular Homogenizer experiments used a very simple volumetric starve feeder. It is a conveyor with a hopper and a variable speed drive (sometimes called the motor control).

The drive speed dial is near the bottom of the scale in the picture below. Unfortunately, this is where the greatest speed variation occurs. The drive is an inexpensive control without even a tach feedback signal. The feed is imprecise. You can watch pellets fall off the conveyor belt. Sometimes no pellets fall off. Sometimes many. This means that the input mass varies significantly. Nevertheless, the pressure is very stable without varying feeder rate or screw speed. This is because of the series of accumulator previously described.

Drive at about 11%

One pellet

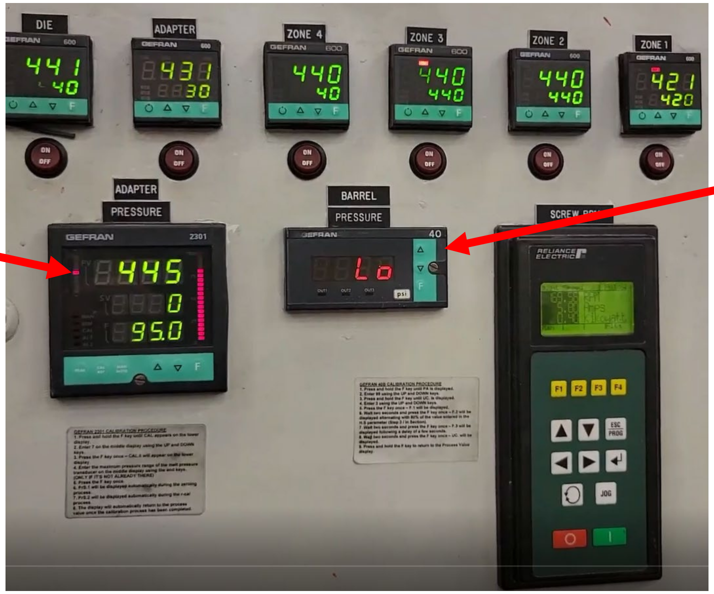
Two pellets

Five pellets

The following procedure was used once the feed rate was set:

1. **Create A Too Starved Screw:** Run the screw at high speed. We typically chose 100 rpm. Run the feeder at a low rate so the screw is excessively starve.
2. **Monitor Two Pressure Gages:** The downstream barrel pressure and the upstream tether ball pressure show the process. When the screw rpm is too fast, the pressure at the end of the barrel will surge because the metering section is not consistently fully. The upstream pressure gage will read zero indicating that the channel is starved as in the picture below.
3. **Slowly Reduce The Screw RPM:** As the screw RPM is reduced, the meter will start to fill more consistently. The operator will see that the lowest point of the surges begins to increase. Eventually, pressure stability will be reached in the plus minus 30 pound range.
4. **Watch The Upstream Pressure Gage:** The upstream pressure gage will read zero. If a low pressure appears on the upstream pressure gage, then raise the screw rpm slightly until it returns to zero.

Downstream Pressure Gage
At Screw Tip

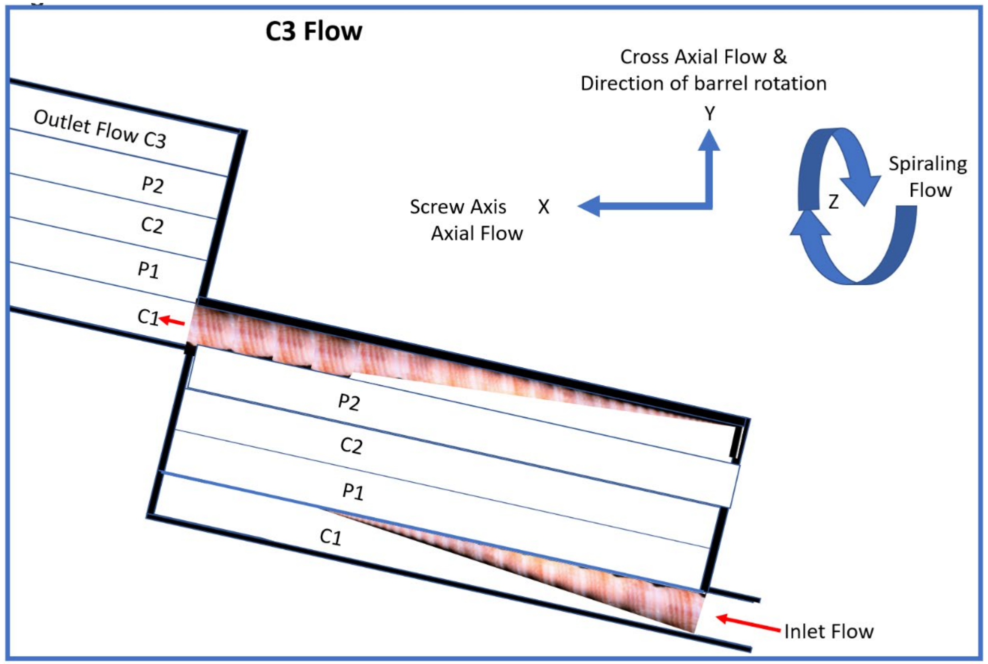


Upstream Pressure Gage

If the feeder were much more precise, say with a loss in weight feeder, then it would also be possible to leave the extruder speed fixed and vary the feeder speed to create the tether ball mixing.

Orderly Three-Dimensional Mixing

While all mixing is three-dimensional, orderliness in three-dimensional mixing is necessary for maximum uniformity. The Molecular Homogenizer is described by assigning three dimensions to a mixing set C1, P1, C2, P2, C3) as in the drawing below:



X Axis Flow C1: The tested Molecular Homogenizer had a series of 2 L/D mixing sets so the length of the spiraling cone above is about 1.5 L/D long. The C1 flow has both an X and Z axis component. The outer part of the flowing cone in C1 is pumped away by P1 leaving the inner material to travel along the X axis. This flow is the axial mixing component. Note that the cone has no pressure flow component. Instead, the flowing cone is in drag flow. This is unlike the flow in the center of a metering section. The axial mixing flow length can be engineered for the requirement. By increasing the P1 pumping clearance, for example, the cone will shorten and the axial mixing will be lessened.

Z Axis Flow C1: The number of spirals can be estimated. In the tested Molecular mixer, the maximum diameter of the tethered ball is about 0.18 inches. The tested 1 inch extruder has a circumference of 3.1/0.18 = ~ 17 revolutions for one barrel rotation (neglecting the frictional drag of the flight). At the small end of the cone, the P1 clearance determines maximum diameter. At 0.04 inches clearance, 3.1/0.04 =~ 78 revolutions per rpm. So, as the material flows down the C1 channel, the number of spirals increase and the pitch of the spirals decrease. The number of spirals can be controlled by the feed rate and the channel geometry.

Y Axis Mixing P1: The material over the P1 pump is in pure drag flow. It has no pressure flow component because the pressure in C1 is near zero. All of the flow over P1 is sheared in an orderly manner. Shear is controlled by the P1 clearance.

Y Axis Mixing C2: The material over C2, no longer having resistance from the P1 surface, is stretched by the barrel into a thin film in a very orderly manner. From cooling experiments, a 0.04 P1 clearance at P1 yielded a film about 0.0014 thick. Limiting the distance from P1 the C3 can limit Y stretching.

Z Axis Flow C3: The Z rotation in C3 is the same direction as in C1. Given the same geometry of the channel as in C1, the diameter and rotations will be the same but ~78 upstream and ~17 downstream per screw rotation. When added together, the entire mass will have rotated equally creating about 95 spirals in a very orderly manner.

C1 and C3 Combined Flow: Eventually, the flow in C1 delivers the outside of spirally cone to C3 where it becomes the inside of the flow in C3. In other words, the outside of mass in C1 becomes the inside of the mass at C3—the mass is turned inside out in a very orderly manner.

Subsequent Mixers:

- **Inversion:** The outside to inside inversion noted above will repeat in the next mixer. The inverted flow will pass through P1, over C2 and eventually regain its original orientation in a very orderly fashion in C3.
- **Comparison To Standard Metering Section:** From the examples above, we see that, within one mixing set, the Z flow creates about 10 times as many spirals as the mixing of a 10 L/D meter where about 1 spiral per L/D occurs. The X axis mixing of a single Molecular Homogenizer set is at least as good as the pressure flow in a metering section. A typical metering section has virtually no Y component like the Molecular Homogenizer stretching over C2. There is no inside to outside inversion of flow in a standard metering section. It seems obvious that each mixing set (C1, P1, C2, P2, C3) mixes at least two orders of magnitude better than a conventional meter. *The tested Molecular mixer serially stacked seven mixing sets.*

Conclusion Three-Dimensional Mixing: One might reasonably think that if each set improves the mix 100 times, that mixing can be very much improved. It seems reasonable that very small molecules, such as water vapor, may not agglomerate into water. While this work has so far concentrated on the mixing of very small molecules, it seems likely that the Molecular Homogenizer can distribute much larger molecules and small particulate better than has previously been possible. As noted earlier, we rate the physical properties based on standard tests that in turn depend on the flaws within the test specimens. When the failure of the test specimens is caused by microscopic agglomerations, better distributive mixing of the flaws can result in improvement in physical tests—essentially improving plastic.

Molecular Homogenizer: Mixing Examples[1]

Coffee Chaff And Oil: Coffee chaff is hygroscopic and contains oil. LDPE and 5% dried coffee chaff, were hand mixed by shaking the materials in a bag. This produced a bubbled extrudate in a conventional single stage screw. Since the material was dried, the oil produced the bubbles. Two atmospheric vents were then used with conventional technology and moderate vacuum. This conventional technology made a bubble free strand for pelletizing.

[1] Sometimes, exacting process conditions (temperatures and screw speed) are required during extrusion for successful operation. For all these experiments, initial temperatures were selected and were not varied. This implies a very robust process unreliant on precision adjustments for effective use.

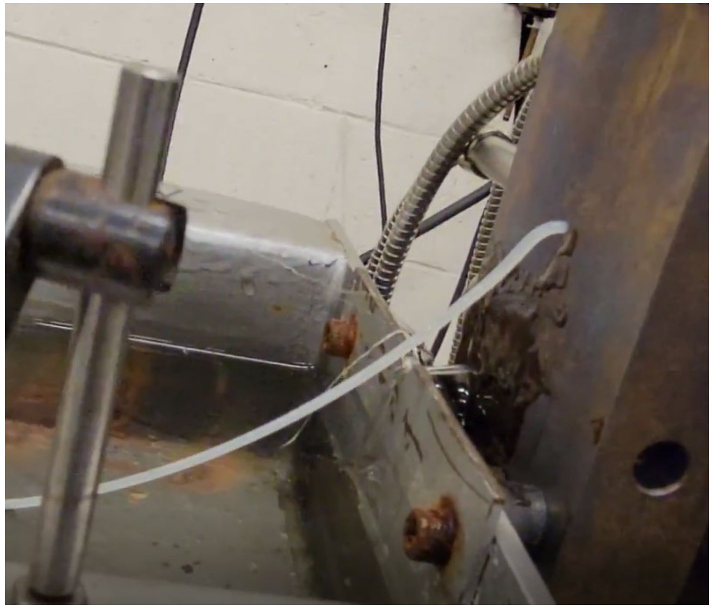
The Molecular Homogenizer was then used in two separate experiments *without venting to compare with the conventional technology.* In the first experiment, 5% undried coffee chaff powder was flood fed. The material foamed, below left.

In the second experiment, the feed was switched from flood to starve feed to induce the tetherball mixing in the Molecular Homogenizer screw. The effect is remarkable as seen in the pictures below:

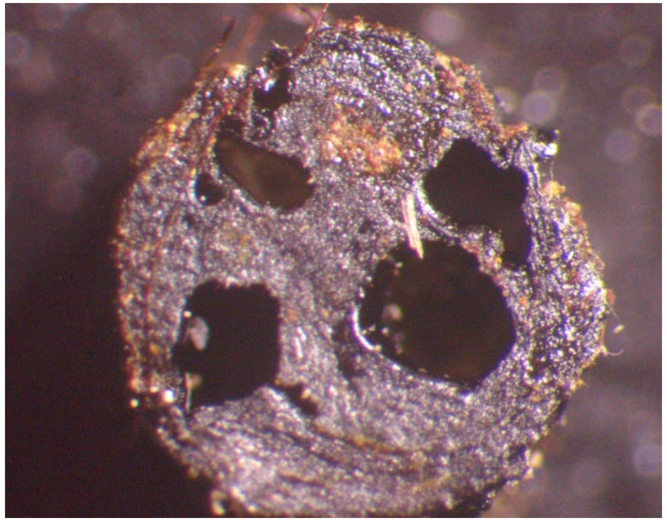
The strand quickly changed from a foam into a bubble free extrudate. The Molecular Homogenizer sequestered the water vapor and the oil. Oils are larger and more complex molecules than water vapor. So, the Molecular Homogenizer worked, not only with very small water vapor molecules, but also sequestered the larger oil molecules. This may bode well for even larger molecules, such as the active drugs used for HME extrusion, where better distribution may have advantages.

PVA Copolymer And Reactive Extrusion: A customer brought an undried hygroscopic PVA copolymer. Processing undried material in a conventional Killion screw produced a bubbled extrudate. The same undried material was processed through the Molecular Homogenizer in tetherball mode and showed no sign of bubbles.

The next experiments were conducted with dried PVA copolymer and organometallics in 3, 6, 9 and 12% for reactive extrusion in the Molecular Homogenizer. The material was in granulated form (3 and 9%) or powder (6 & 12%). At 3% there were no signs of bubbles below right. Initial residence time of some color concentrate pellets was measured as 132 seconds.



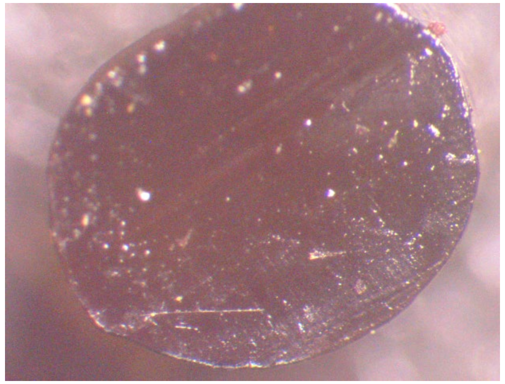
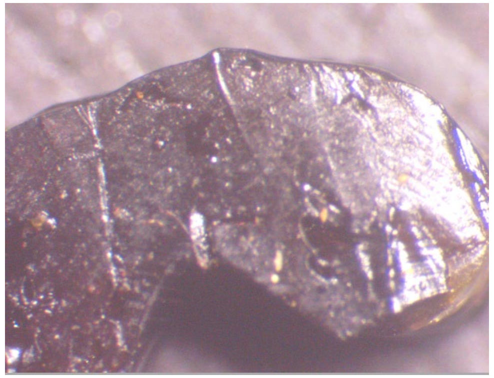
At 6%, bubbling occurred, left below. The customer had also found that at 6%, bubbling occurred and sent an iodine stained cross section, below right, from his Killion extruder.



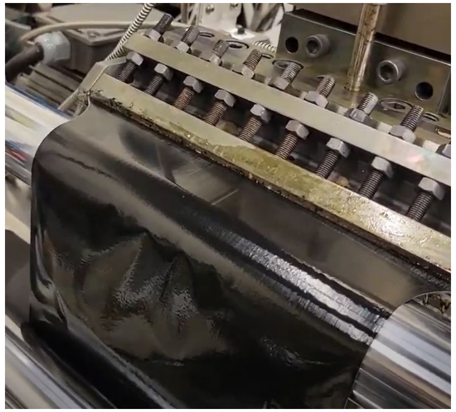
An atmospheric vent was opened over the Molecular Homogenizer screw. Bubble free extrudates were then produced at 6, 9 and 12%, left to right below. There are no signs of bubbles. The customer estimated that as much as 1.5% of the polymer may have been converted to a gas at 12% organometallic during the reactive extrusion.



The customer sent two iodine-stained cross strand sections at 9% and 12%, left to right below. There are no signs of bubbles indicating that the atmospheric venting was successful.

SAN (Styrene-acrylonitrile) Color Concentrates: SAN is hygroscopic. Color concentrates used to color polymers often have a significant amount of pigment and surface moisture. Undried SAN color concentrate (containing 4% pigment) was processed through a conventional screw in a cast film line as a control. The material produced is typical of undried hygroscopic material and resembles a net more than a film, left top TIO2, left bottom carbon black. The same undried SAN color concentrates were processed through the Molecular Homogenizer, a water trough, strand pelletizer and into pellets, center top TIO2, center bottom carbon black. There were no sign of bubbles. These undried pellets were extruded in the same cast film line as the control. No sign of bubbles. It is interesting that the mixedness of the pellets was retained from the Molecular Homogenizer in the control screw.



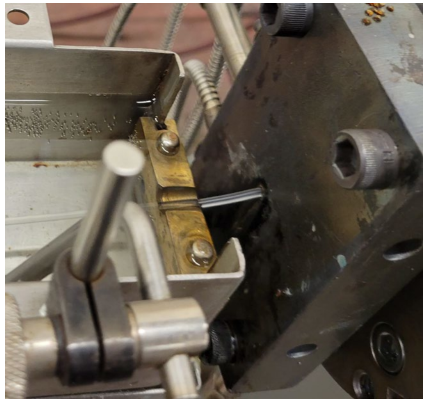
PMMA:

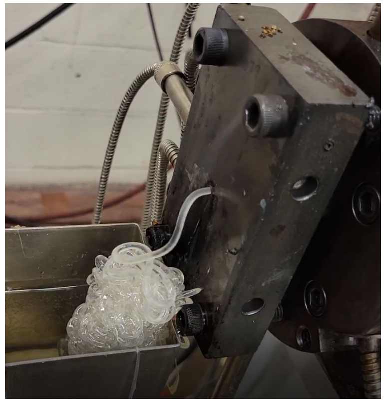
- **Undried Material:** A non-bubbled strand was produced and pelletized by the Molecular Homogenizer.
- **Mixedness Retained In Dried PMMA:** Dried material was processed through the Molecular Homogenizer, a water trough and strand pelletizer. The material was left exposed to atmosphere for three days and then processed through a conventional screw. There were no sign of bubbles, below left. This is not normal. Typically, you would see bubbles in 4 to 6 hours.

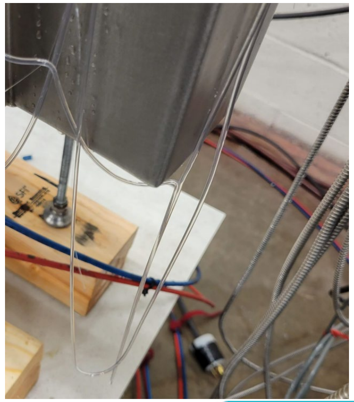
- **Direct Extrusion:** This is the twin screw term for making a product while mixing in the twin. As outlined previously, a gear pump is used with the CRTS twin to build the required stable pressure. It is not necessary for the single screw Molecular Homogenizer as shown in the undried PMMA cast film line, above right, making a 1 mil cast film.

PEEK: PEEK is a high temperature hygroscopic material. Undried PEEK was processed through the Molecular Homogenizer, stranded and pelletized. There was no sign of bubbles.

Polycarbonate: Undried polycarbonate was processed through the Molecular Homogenizer. There was no sign of bubbles in the melt, left. Slow cooling center, right gives more time for bubbles to develop if present but none are seen.

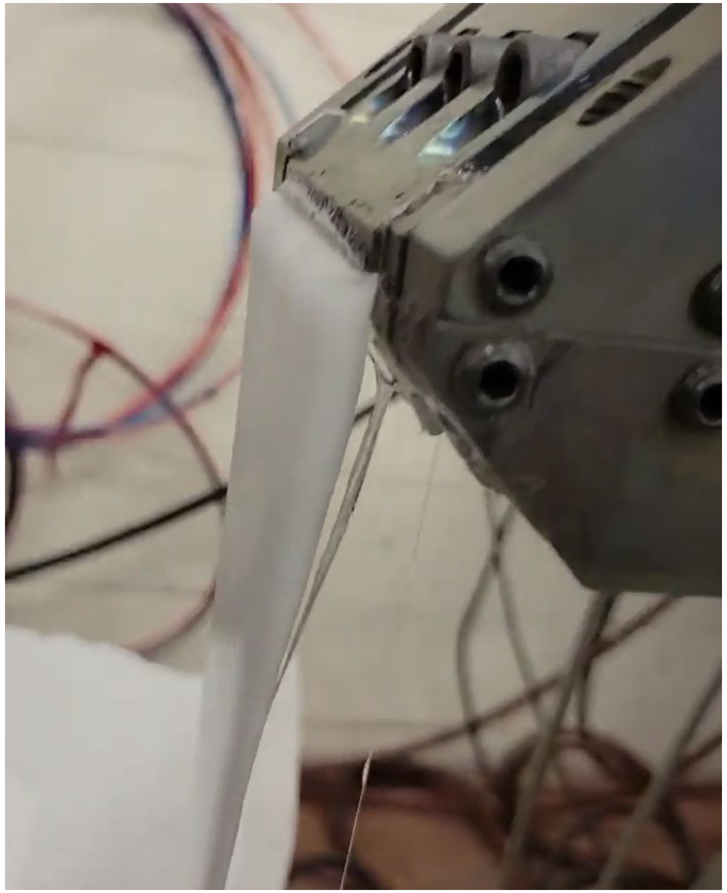






Foam Mixing: Chemical blowing agents are mixed with various polymers to reduce the density of the extrudate. A typical concentration of 1 to 1.5% of the blowing agent is often required. The process often requires exacting temperatures as the blowing agent pellets must not gas too soon in the screw or the gas will flow out the hopper. This requires flood feeding to make an upstream seal against gas escape. The gas must also be sufficiently cool at the extruder discharge so that the bubbles do not burst leaving the die.

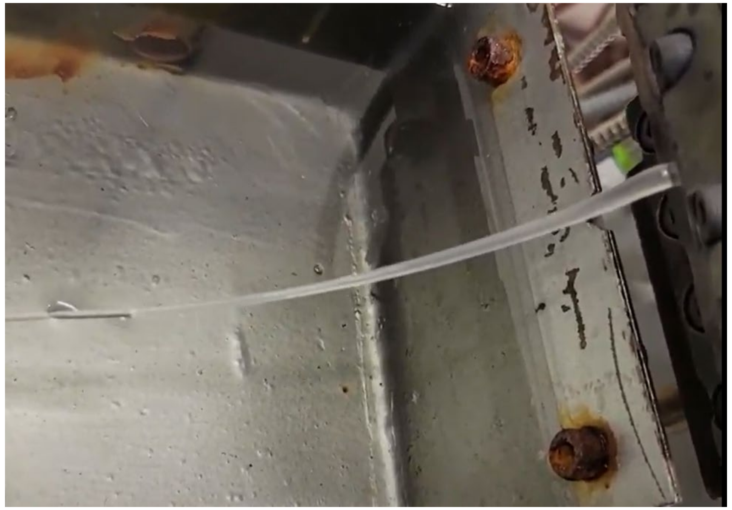
An experiment with a conventional screw and a customer's proprietary material was found to expand sufficiently with 1.5% blowing agent on a control screw. At the same conditions, the Molecular Homogenizer required only 0.5% of the chemical blowing agent to produce the same result. The implication is that the Molecular Homogenizer mixed to a much finer scale in a flood fed application.

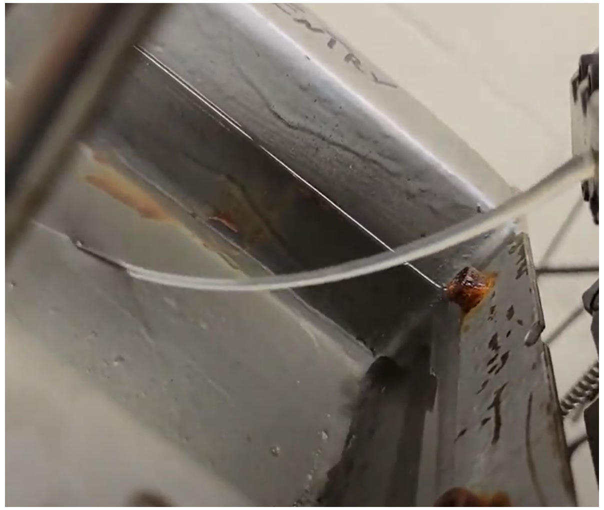


PET:

- **Undried PET:** PET is well known as a very hygroscopic material. Undried crystal PET was processed in the Molecular Homogenizer and no bubbling was visible, below left. The material was pelletized and so transformed into the amorphous form, center.
- **Undried PET With 25% Amorphous PET:** The pelletized material above, now in the amorphous form, was hand mixed with the undried crystalline form to simulate the introduction of reclaim PET without drying. No bubbles were seen in the mixture, right.

This is not to imply that the PET did or did not chain scission. Near term testing is scheduled to determine if there was a viscosity drop.





CONCLUSIONS

The Molecular Homogenizer uses a novel mixing mechanism that has an orderly structure. It organizes materials in three dimensions. Each mixing set (C1, P1, C2, P2, C3) is capable of order of magnitude improvements in mixing compared to the standard metering section. The ability to keep water vapor from agglomerating into water implies an unprecedented mixing ability. This has implications for physical property tests and polymer improvement. Each part of the organizing structure can be engineered as required to alter X, Y and Z.

This paper has shown that the Molecular Homogenzer:

- **Sequesters:** Water vapor in all the undried hygroscopic materials tested.
- **Sequesters:** Water vapor in undried hygroscopic material and sequesters oil at the same time in the coffee trial.
- **Sequesters:** Water vapor in undried hygroscopic material and surface moisture in color concentrates at the same time.
- **Sequesters:** Gas during reactive extrusion during venting.
- **Processes A Broad Material Range:** The materials processed represent a wide range of polymer families.
- **Has Ease of Processing:**
  - **Robust Processing:** Typical process temperatures were used. There was no need to alter them.
  - **Ease of Use:** Following the standard procedure, it was easy to induce tetherball mixing.
  - **Pressure Stability:** All materials were processed on the same screw; all were found to maintain very stable pressure.
- **Gas Removal:** An atmospheric vent over the Molecular Homogenizer screw showed impressive venting ability.
- **Foaming:** Far less chemical blowing agent was required in the Molecular Homogenizer to produce a foam similar to the conventional control screw.
- **Little Temperature Rise:**
  - **Drive Amps:** An empty screw used 5.6 amps to turn the screw. The drive’s shutdown amps were 13. The motor amps required to mix were 5.8 to 6.1. This indicates very low energy input from the drive as might reasonably be expected to rotate a melted ball.
  - **Melt Temperature:** It is difficult to accurately measure the melt temperatures but an infrared gage yielded about the same temperatures as the last barrel zone setting which is typical of a small extruder. It never reported a significant temperature rise.
- **Mixedness Retained:**
  - **Conventional Screw:** A molecularly homogenized mixture retained the sequestration of water vapor and surface moisture in a conventional screw in color concentrates and PMMA.
  - **Conventional Screw:** Mixedness of dried PMMA showed no sign of bubble after three days of exposure to atmosphere in a conventional screw.