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# Compression Molding of Ultrafine TATB with Various Mold Releases (#13903)*

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# A processing issue caused us to investigate the compression molding of two detonator grade explosives

We investigated:  PE, LLM-105 and UF TATB compaction and extraction

1. 13 proprietary MRs based on PTFE, Silicone, and Wax
2. The effect of different mold releases (MR) on compaction of UFTATB
3. The densification process, stress relaxation and spring-back
4. The extraction process: force/pressure as parts were extracted for different mold releases

We modeled the compaction process with 3 simple models

1. Walker-Bal'shin → $\rho$ or $\rho_r = C_1 + k \log(P)$
2. Heckel → $\ln[1/(1-\rho_r)] = K*P + A$
3. Kawakita – Ludde → $P/C = P/a + 1/ab$ where $C=(V_o - V)/V_o$

Models are single cycle compaction with no effects of different rates, cyclic loading, binder or temperature.  Most of the work was done on one lot of ultrafine TATB to minimize particle size and lot-to-lot variations

Proof out testing was done with inert pentaerythritol (PE) fine particles to simulate UF TATB



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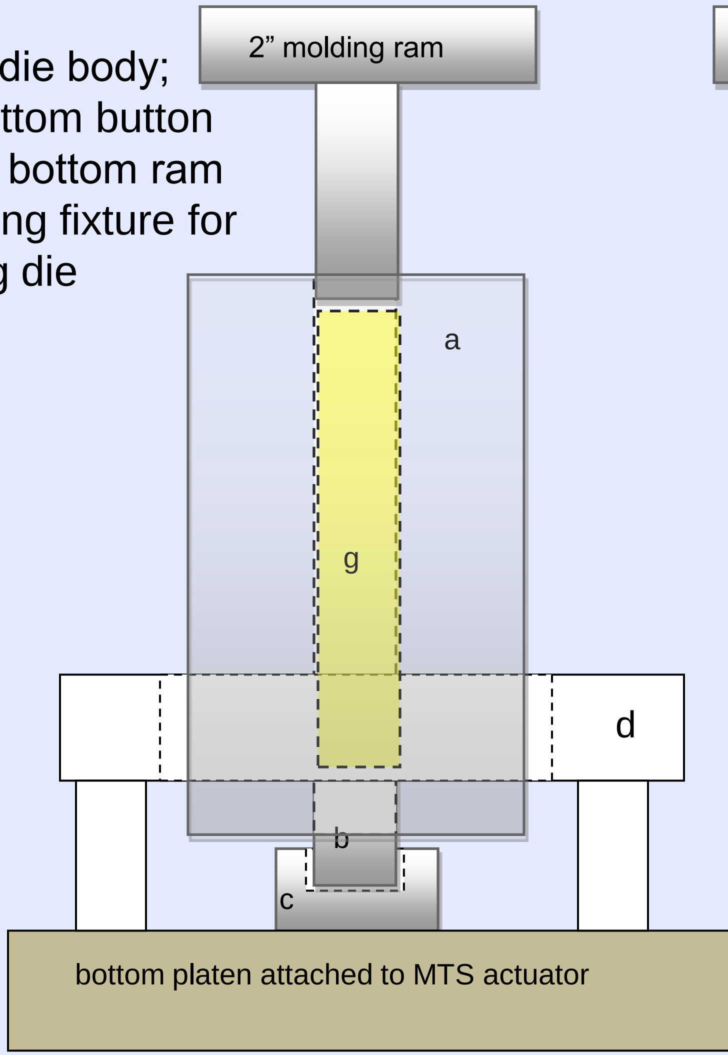
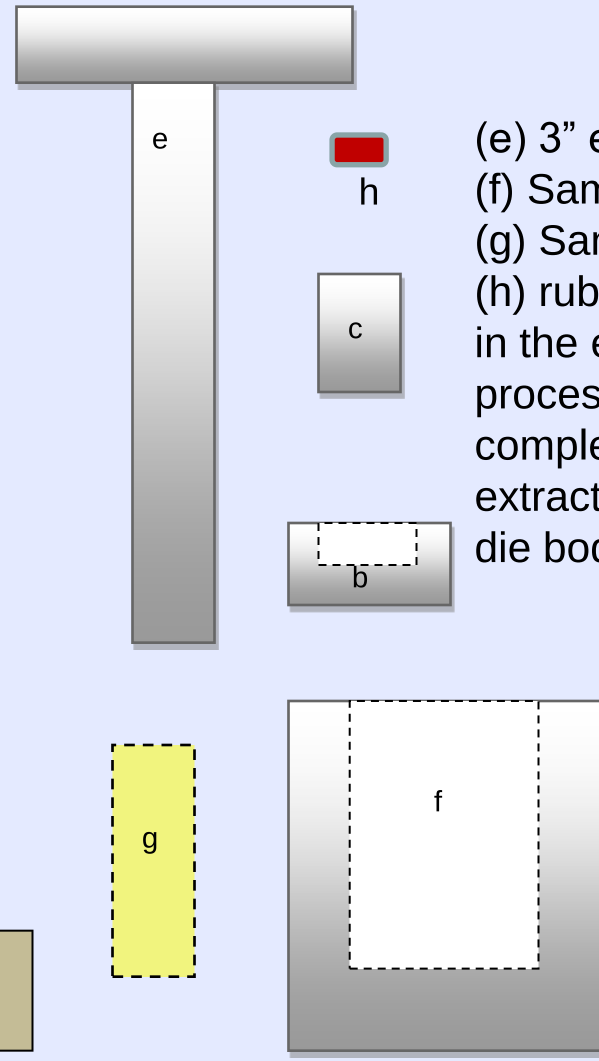
# Compression molding test setup: Extraction test set:

(a). 3" die body;
(b). Bottom button
(c). ¾" bottom ram
(d). Ring fixture for holding die




(e) 3" extractor ram
(f) Sample catcher
(g) Sample
(h) rubber button used in the extraction process to prevent complete closure of the extraction ram on the die body.



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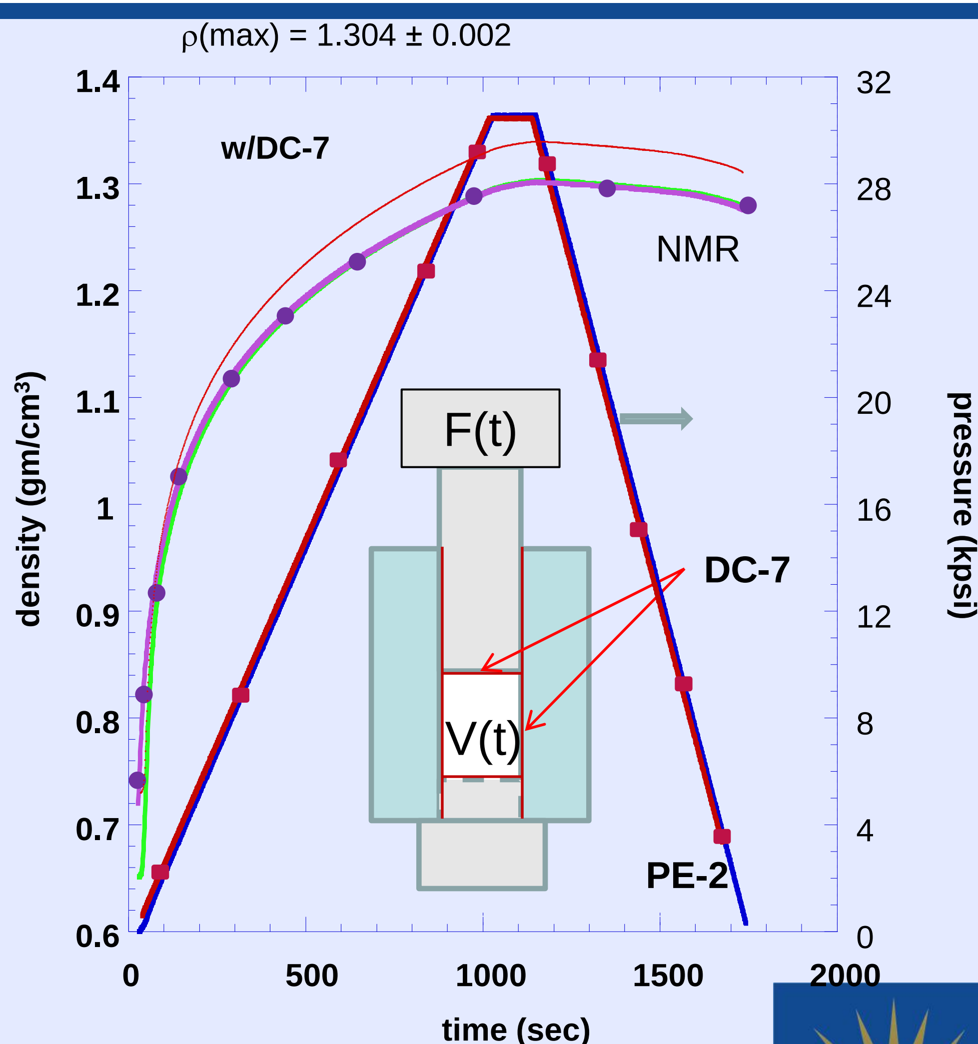
# Developmental testing was done with inert pentaerythritol (PE) fine particles to simulate UF TATB

1. Two pentaerythritol samples were pressed from bulk density of about 0.6 to final density of 1.266 ±0.001 gm/cm$^3$ without MR (excellent reproducibility)
2. Load control ramp at 6 lb/s to 6000 lbf ~ 30 ksi; hold 2 min at 6000 lb; ramp down at 10 lb/s
3. Single ramp
4. Use DC-7 MR on ram and die increased density to 1.281 gm/cm$^3$




*A significant increase in part density was observed w/ MR*



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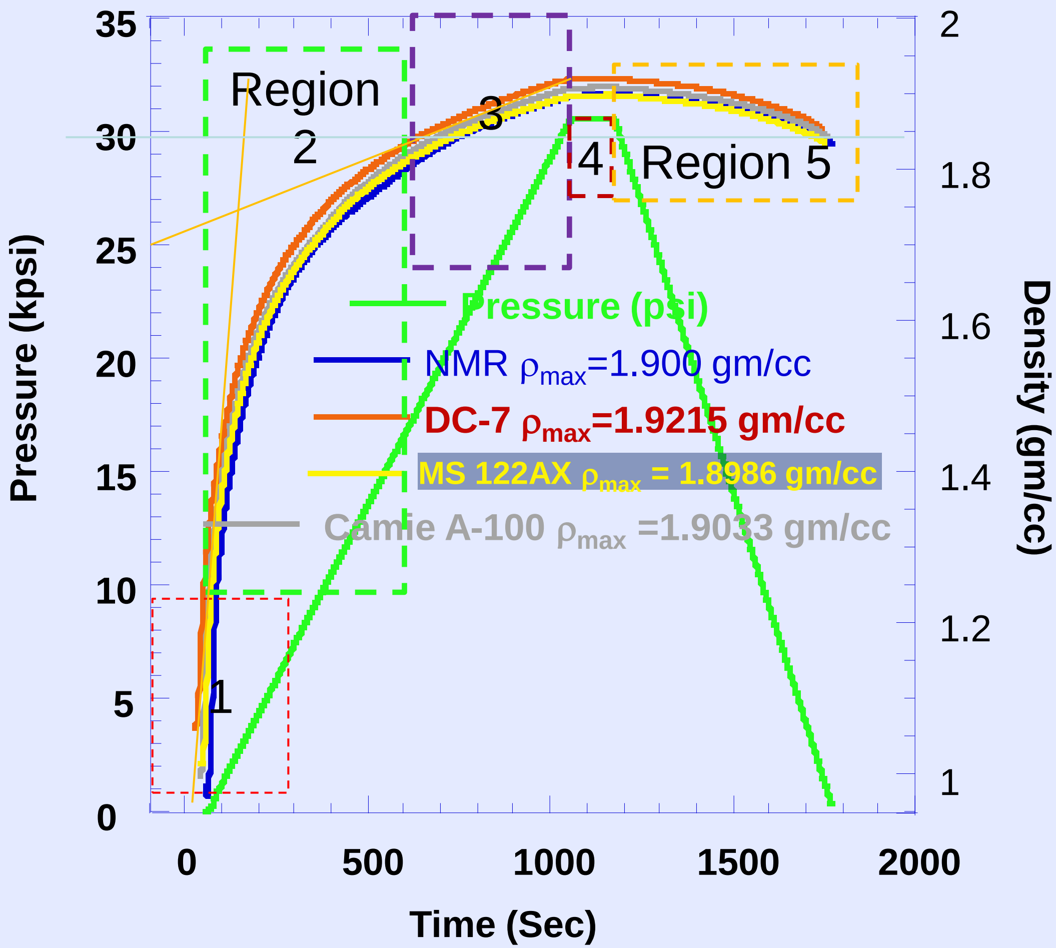
# Varying MR has only small effect on single cycle compression of UF TATB to 30 ksi

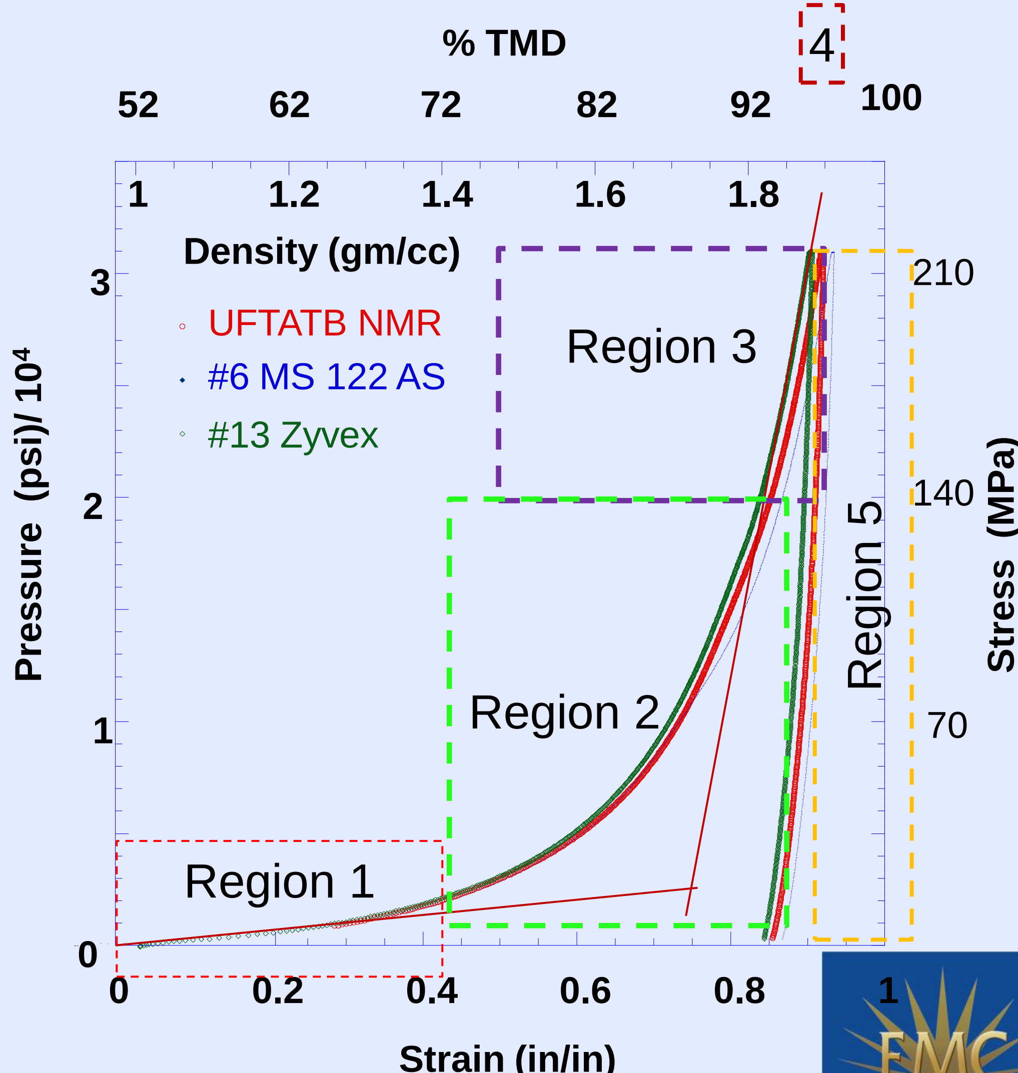
- No mold release (NMR) pressure density trace was similar to all mold release traces
- Significant spring-back reduced density from ~1.9 to 1.83 gm/cc independent of MR
- Spring-back from 30 ksi to 70 psi was 35 mils or about 3.5%




*No effect of MR on density –pressure traces may be associated with low friction coefficient of UF-TATB*

# Considering stress – strain plots (pressure-density) shows the usual steps in powder compaction

1. Initially at tap density, small ΔP increase the density quickly void filling. 50-75% TMD
2. Above ~300 psi (1.8 MPa) rapid densification slows down as particles get in each others way
3. Above 2 ksi (140 MPa) void volume has been filled, particles yield and flow; density increases from 90-95% TMD.
4. During 2 m hold small density increase
5. As pressure is released the part springs back (expands) ~ 3-4%





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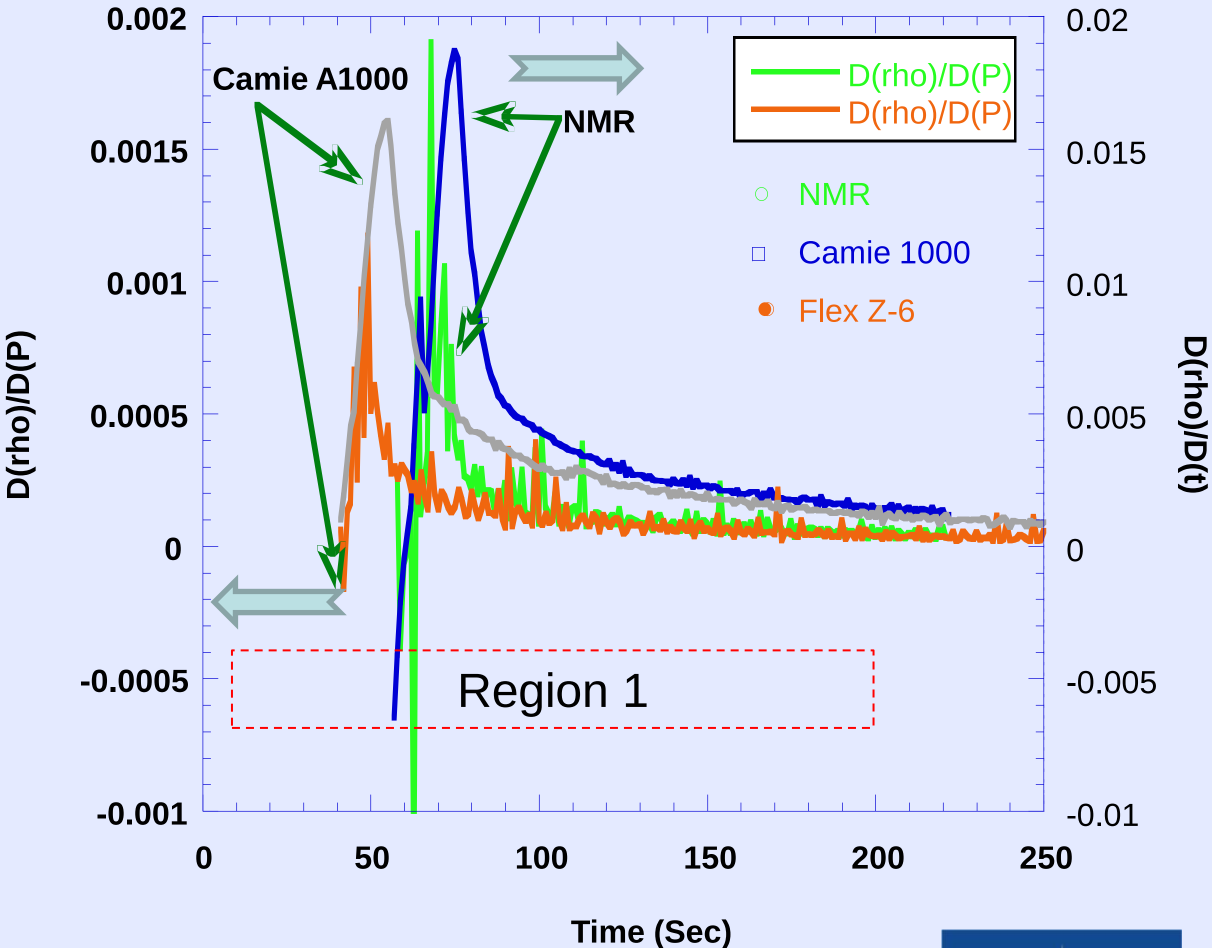
# The rate of change of density with pressure (time) passes thru a maximum very early on during the compaction

Region 1 – void filling is complete very quickly

The time derivative is smoother but the effect is the same.

The maximum occurs in the first 1-2 minutes in all cases.

This corresponds to not much more than a couple hundred psi




*This region is neglected in the simple compaction models*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# Walker-Bal'shin plots of UF TATB with various release agents showed 3 regions 1, 2 and 3 very well.

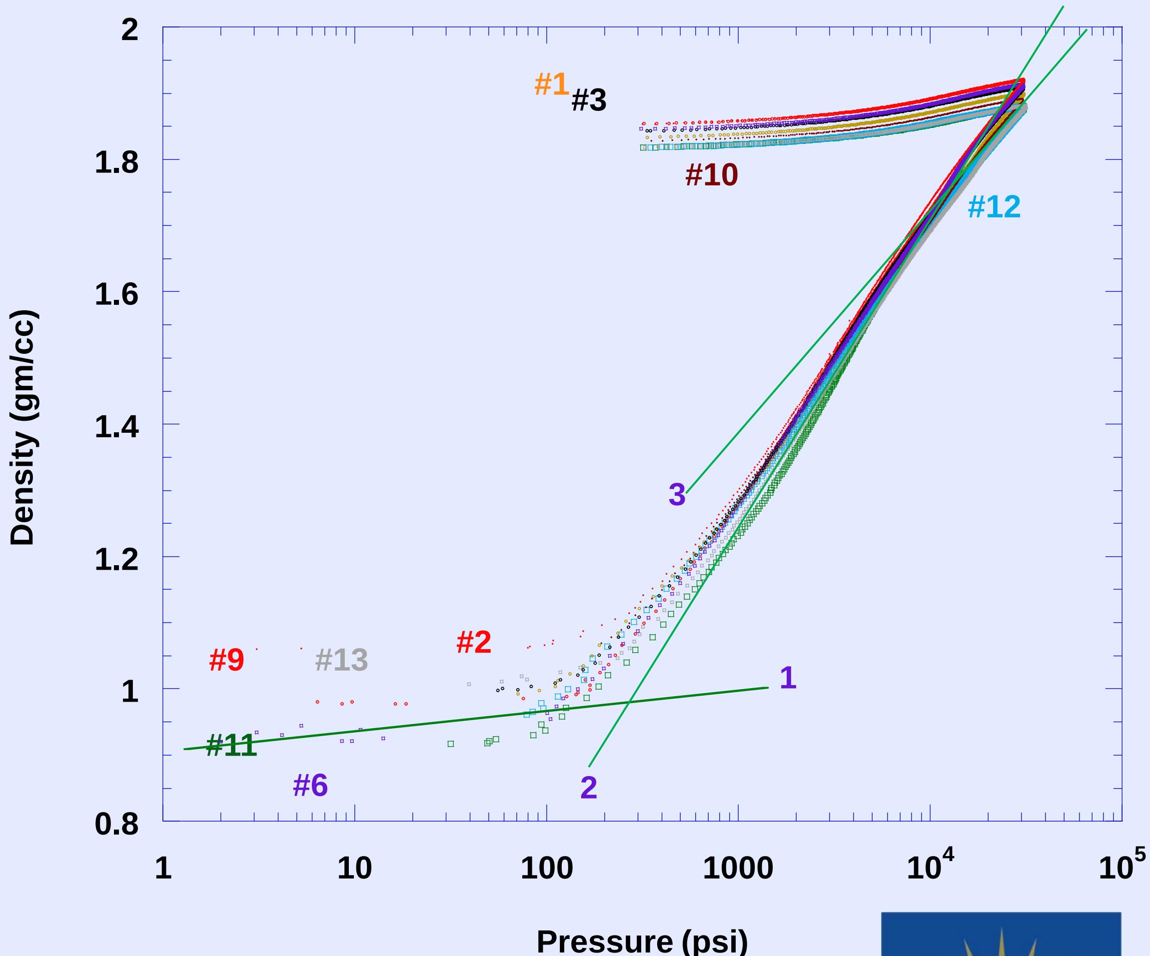
Walker-Bal'shin

$\rho$ or $\rho_r = C_1 + k \log(P)$

- Should be log linear in P

Obviously not, implies 3 compaction regions:
1 → C1~.81; k~0.077
2 → C1~-0.122; k~0.461
3 → C1~0.25; k~0.372

Question: Is R2 mostly fracture and R3 mostly yield, flow and adhesion?




*UF TATB doesn't follow simple Walker-Bal'shin*



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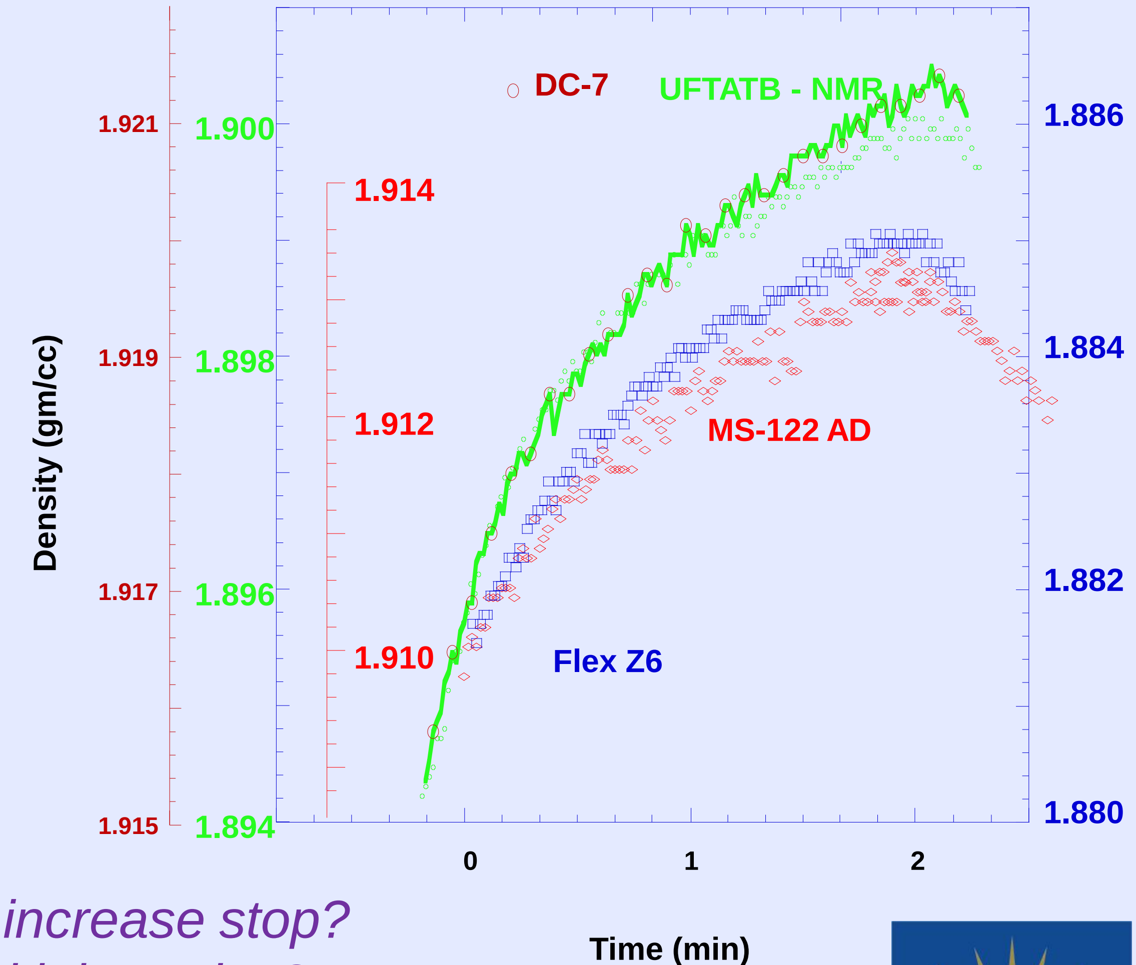
# What happens during the 2 minute hold? There is no time dependence in the models so nothing should happen.

Regime 4

1. The density continues to increase slightly during the constant pressure hold
2. It takes longer than 2 minutes to equilibrate
3. There seems to be some effect caused by different mold releases
4. Density increase is small ~(0.2-0.3%)



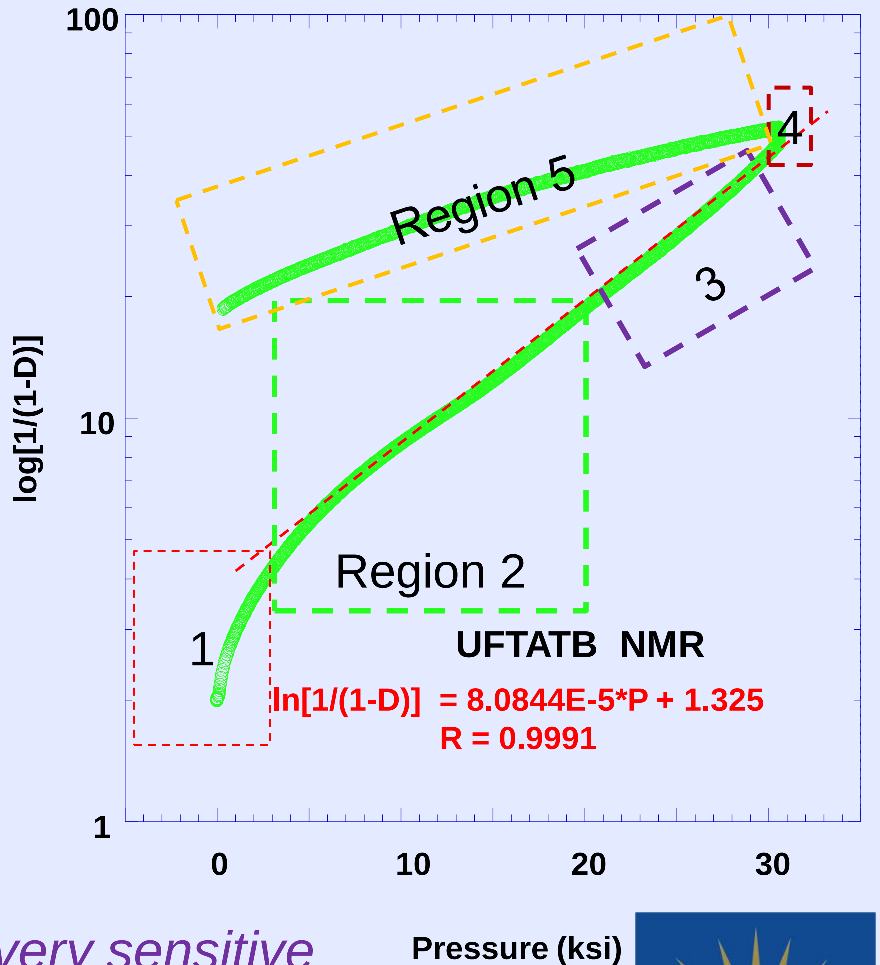

*When does the density increase stop?*
*What is the effect of multiple cycles?*

# The Heckel equation was applied only to the "linear" section of the compaction curve (5000-30000 psi)

Heckel Equation for compaction:

$\ln[1/(1-D)] = K*P + A$

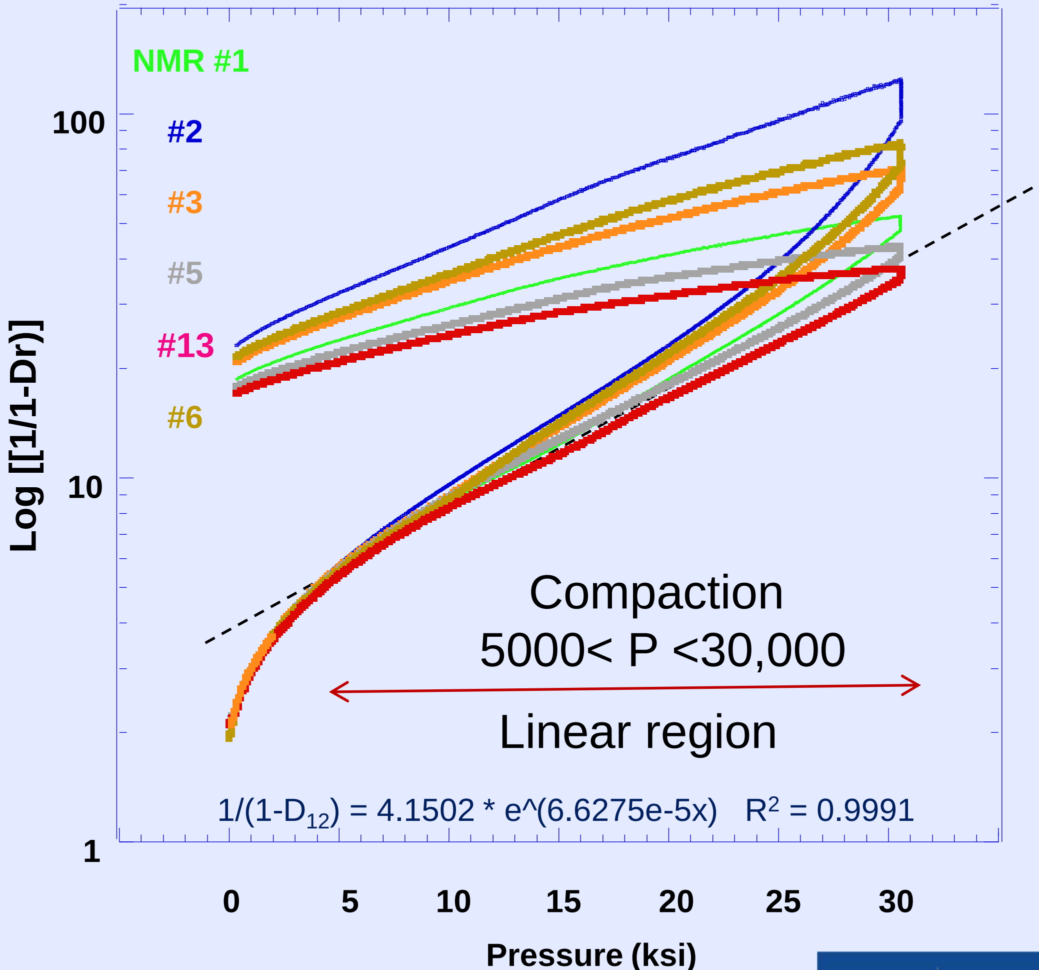
Where D = relative density
K= slope of straight line portion
K~1/ <$P_y$> mean yield pressure
D = the relative density
= den(P)/1.937 (TMD)
K(linear portion) = 8.0844E-5
A(5000-30000 psi) = 1.325
$D_a$ = relative density of A = $1-e^{-A}$
$D_a$ = 0.7342 (where particle deformation begins)
$P_y$ = 1/K = 1.1357 ksi = 7.83 MPa




*1/[1-(ρ(P)/TMD)] ~ 1/void fraction – very sensitive near TMD – shows density increase in region 4*

# Plotting different MRs using log (1/1-Dr) vs P (Heckle) separates the different release agents, but it's unclear why.

| ID # | $P_y$ * (MPa/ kpi) | $D_a$ (%) |
|---|---|---|
| 1 | 85.3 (1.24) | 73.4 |
| 2 | 69.8 (1.01) | 71.0 |
| 3 | 77.8 (1.13) | 70.3 |
| 4 | 86.0 (1.25) | 73.8 |
| 5 | 94.0 (1.34) | 75.8 |
| 6 | 72.9 (1.05) | 70.3 |
| 7 | 75.8 (1.10) | 72.0 |
| 8 | 82.0 (1.19) | 74.6 |
| 9 | 67.4 (0.98) | 68.4 |
| 10 | 91.2 (1.32) | 74.4 |
| 11 | 104.6 (1.5) | 76.8 |
| 12 | 104.0 (1.5) | 75.9 |
| 13 | 97.5 (1.41) | 74.8 |




Particle deformation begins ~85 ± 12 MPa (1.2 ± 2 kpi) and 73 ± 2% TMD)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# Kawakita-Ludde Equation fits the data very well

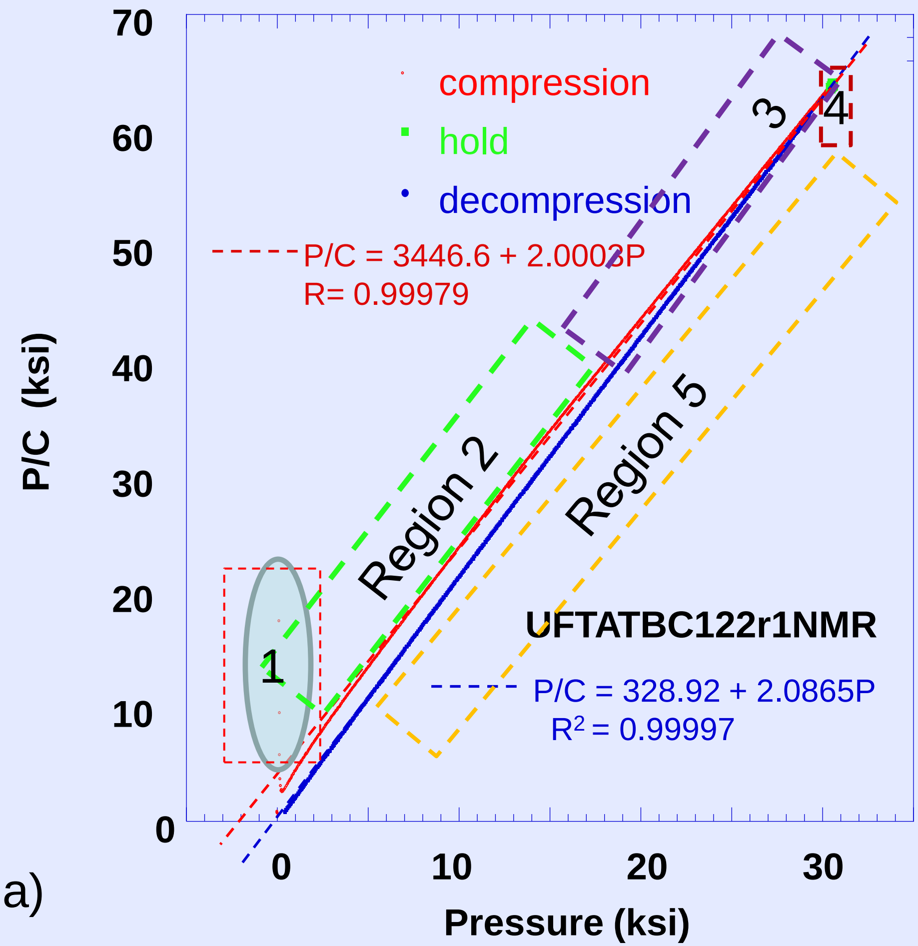
Kawakita Equation for compaction:

$C = (Vo-V)/Vo = abP/(1+bP)$

Rearranging:

$P/C = P/a + 1/ab$

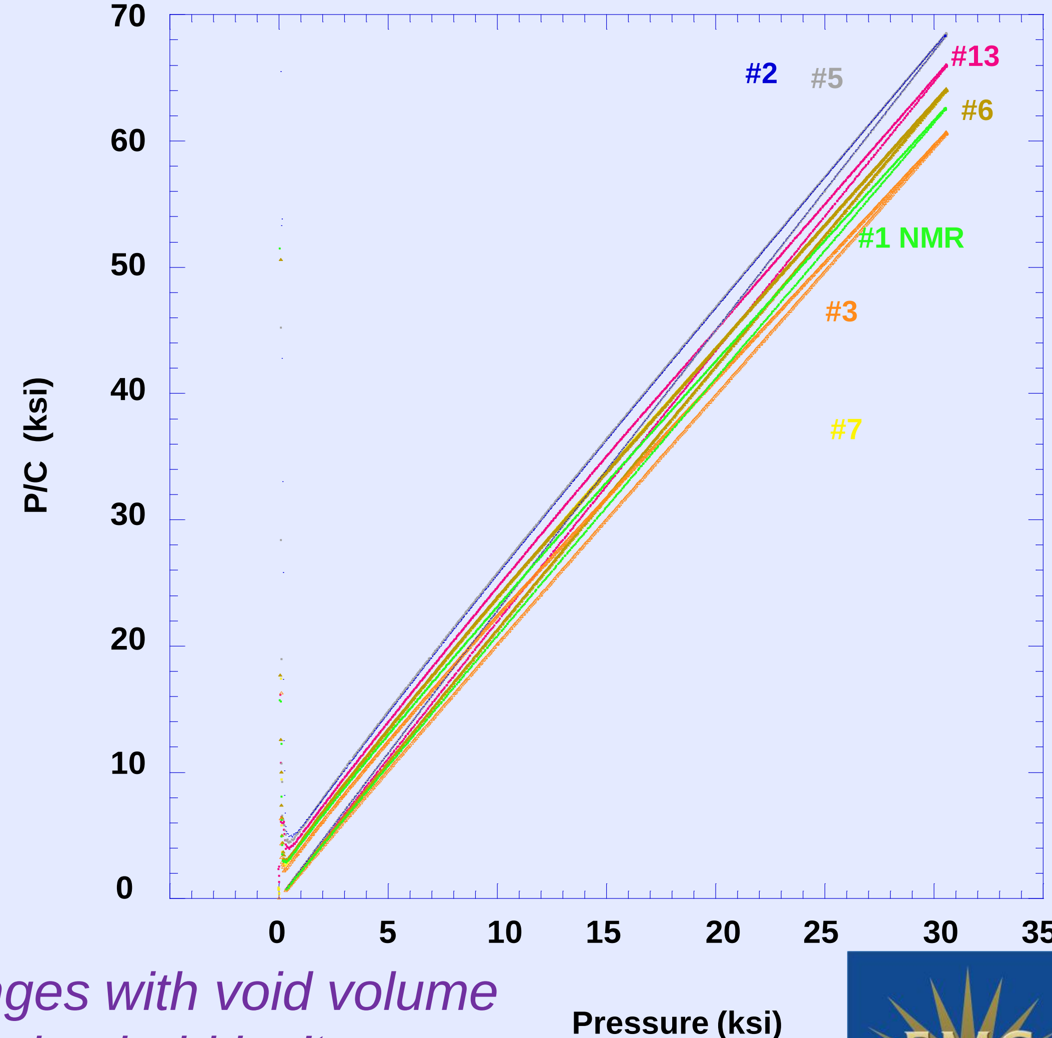
Where Vo = initial volume,
P = pressure
1/a = slope = 2 or 2.087; a~ 1/2
$1/b = P_k = P(50\%\ \text{compact})$
$P_k$ = 6900 psi = 47.5 MPa
Compaction and release curves look similar; no effect of hold
1/b(decomp) = $P_{kd}$ = 686.3 psi (4.73MPa)




*Note that initially the compaction trace is noisy and doesn't fit the least-squares line*

# Kawakita plots for 6 different MRs showed some variation with different mold release agents

- •Compaction:
  - Anomalous early compaction behavior
  - 50% compaction pressure (1/b) averaged 50±10 MPa (7300 ± 1500 psi)
  - The 50% compaction pressure corresponds to around 85% TMD in the part
- •Release:
  - •Slope → P(50%) = 2-3 MPa (3-400 psi)




*Because this equation changes with void volume the small density change during hold isn't seen*



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# 13 different mold releases were evaluated based on compaction and extraction behavior with UF-TATB

| Test # | Mold release | Type | Density (gm/cc) | Measured (gm/cc) | Manufacturer |
|---|---|---|---|---|---|
| 1 | none | | 1.8333 | 1.8376 | |
| 2 | DC7 | Silicone | 1.8532 | 1.8420 | Dow Corning |
| 3 | Camie 1000 | Oligomer fluorocarbon | 1.8427 | 1.8421 | Camie-Campbell, Inc |
| 4 | MS 122AX | Oligomer fluorocarbon | 1.8334 | 1.8465 | Miller-Stephenson |
| 5 | Eject-it E28 | Fluorofilm Dry Coat | 1.8272 | 1.8435 | Price-Driscoll Corp |
| 6 | MS122AD | Oligomer fluorocarbon | 1.8458 | 1.8514 | Miller-Stephenson |
| 7 | MS122DF* | Oligomer fluorocarbon | 1.8466 | 1.8499 | Miller-Stephenson |
| 8 | Krytox | Oligomer fluorocarbon | 1.8431 | 1.8470 | IMS |
| 9 | S-202 | Spherical Talc | 1.8536 | 1.8483 | Silverline |
| 10 | N-99 | Platy Talc | 1.8283 | 1.8489 | Nytal |
| 11 | Premium U/PAR | Paintable mold release | 1.8183 | 1.8513 | Price-Driscoll |
| 12 | Ultrall sili | Silicone | 1.8179 | 1.8455 | Price-Driscoll |
| 13 | Zyvex Flex-6 | 3 part Wax treatment | 1.8222 | 1.8339 | Zyvex, Inc |

*Average density = 1.836 ± 0.013 ; 1.845 ± 0.005 (flash?)*



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# Comparison of UF parts prepared from 13 different mold releases show a density reduction of about 2.9%±0.75

- Density at maximum pressure was 1.901±0.014 gm/cc
- Measured density of extracted parts was 1.845±0.005
- No significant differences in compaction or density results

| ID | ρ(bulk) | ρ(0) | ρ(max) | SB(%) | Δρ(SB) |
|---|---|---|---|---|---|
| 1 | 0.984 | 1.8376 | 1.9 | 3.28% | 0.0667 |
| 2 | 1.06 | 1.8420 | 1.9215 | 4.14% | 0.0683 |
| 3 | 0.998 | 1.8421 | 1.9093 | 3.52% | 0.0666 |
| 4 | 1.015 | 1.8465 | 1.8986 | 2.74% | 0.0652 |
| 5 | 1.047 | 1.8435 | 1.8917 | 2.55% | 0.0645 |
| 6 | 0.938 | 1.8514 | 1.9134 | 3.24% | 0.0676 |
| 7 | 0.979 | 1.8499 | 1.9117 | 3.23% | 0.0651 |
| 8 | 1.042 | 1.8470 | 1.9064 | 3.12% | 0.0633 |
| 9 | 0.980 | 1.8483 | 1.9206 | 3.76% | 0.067 |
| 10 | 1.069 | 1.8489 | 1.8919 | 2.27% | 0.064 |
| 11 | 0.916 | 1.8513 | 1.8808 | 1.57% | 0.0625 |
| 12 | 0.961 | 1.8455 | 1.8805 | 1.86% | 0.0626 |
| 13 | 1.007 | 1.8339 | 1.885 | 2.71% | 0.0628 |


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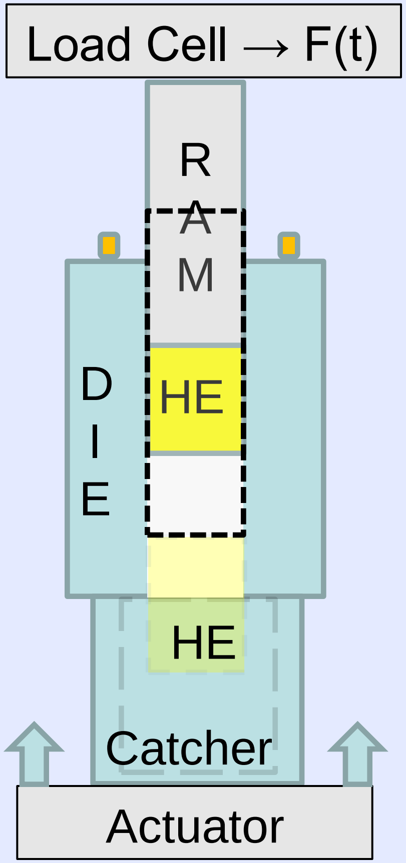
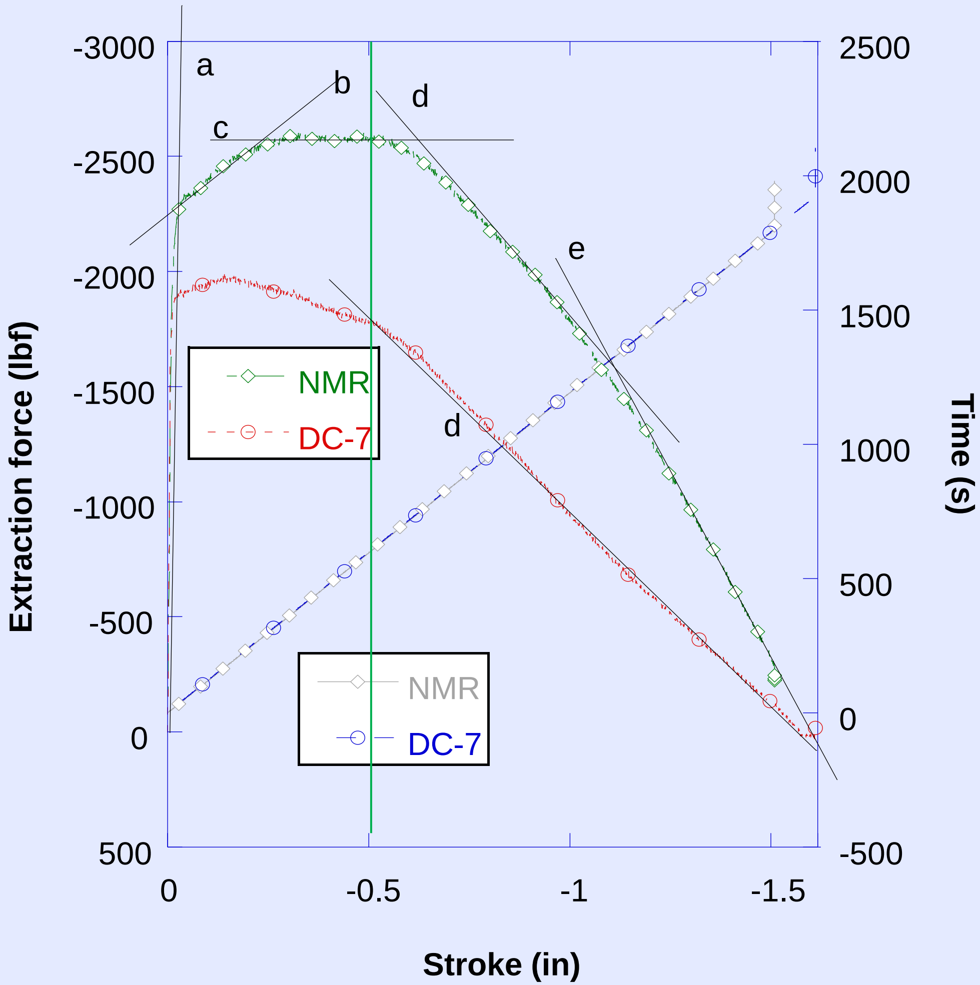
# The extraction process was monitored by load cell and position of the actuator as the part moved out of the die

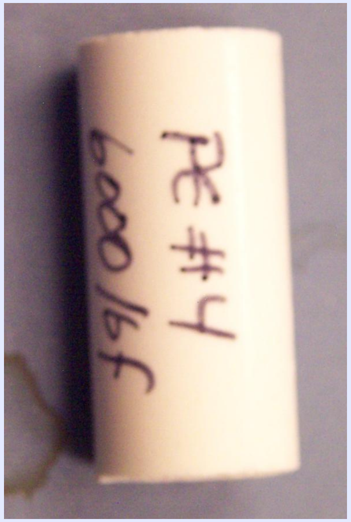
1. Ram and bottom insert removed
2. Rubber stoppers inserted between die body and extracting ram  to prevent bottoming out.
3. In stroke control mode actuator was raised at 0.05 in/min until part is pushed into catcher (~1.5” with ~ 1” part requires about 30 min to extract.
4. Actuator position and load were measured during the extraction process.
5. PE Extracting load increased rapidly to about 2300 lb (~12 ksi), then slowly for about 0.2 in and became nearly constant at about 2600 lb (13.3 ksi)
6. After ½ “ motion, the part begins to exit the die and the force drops off

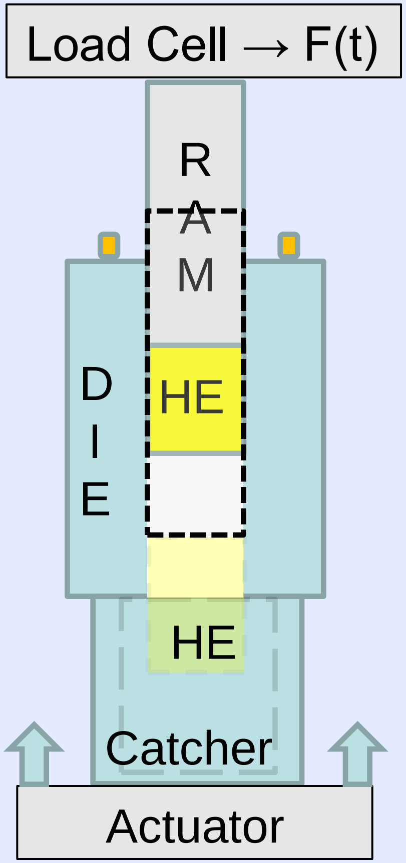



*Follow extraction force on part in die with or without MRs*

# Significant reduction in extraction force with DC-7 mold release with pentaerythritol



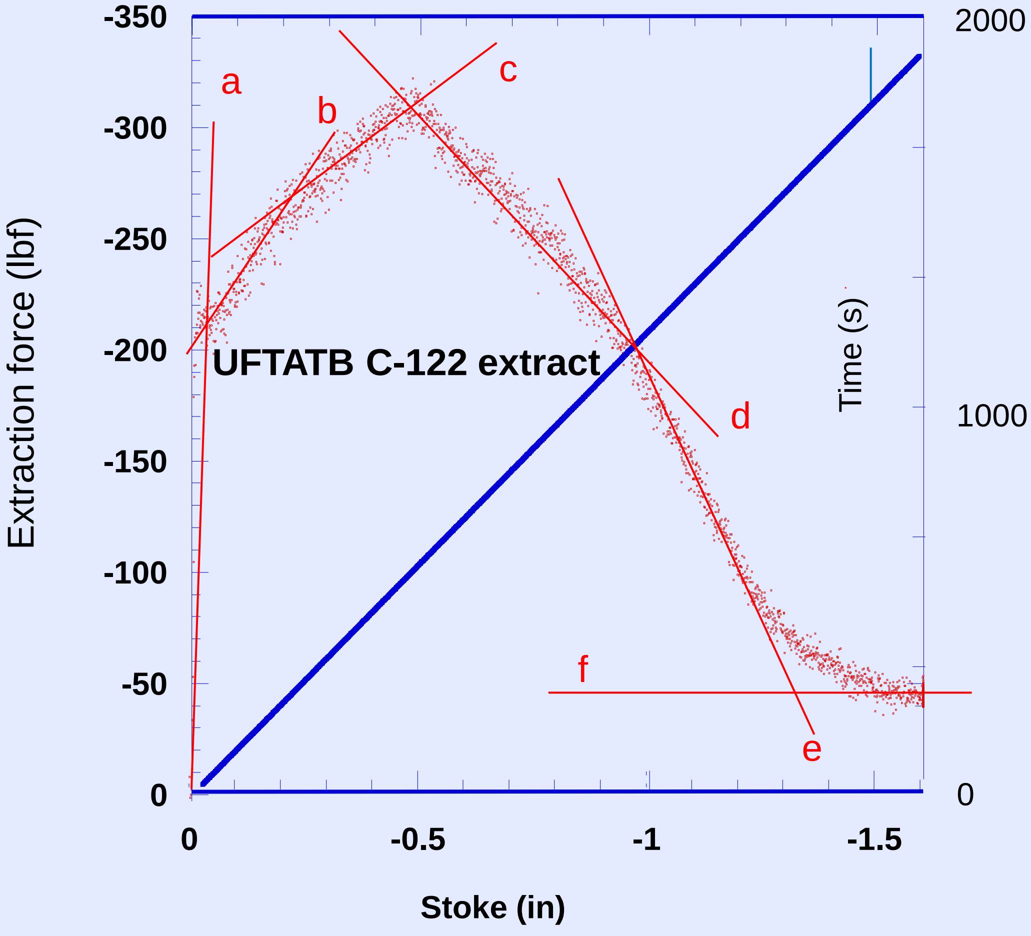




Even with mold release PE “chipped” on extraction

# UF TATB extracted easily compared to PE but stages were similar

1. Only ~320 lb-f required to extract UF TATB compared to 2600-2000 lb-f for PE
2. $F_e$ change steps:
   - a. Rapid increase initially until part starts to move
   - b & c. Increases in 2 steps until part begins to exit the die.
   - d & e. constant decreasing rate until part is ½ way out of the die than faster rate
   - f. When part exits die $F_e$ becomes constant.




*Why is the extraction force so much lower for UF TATB?*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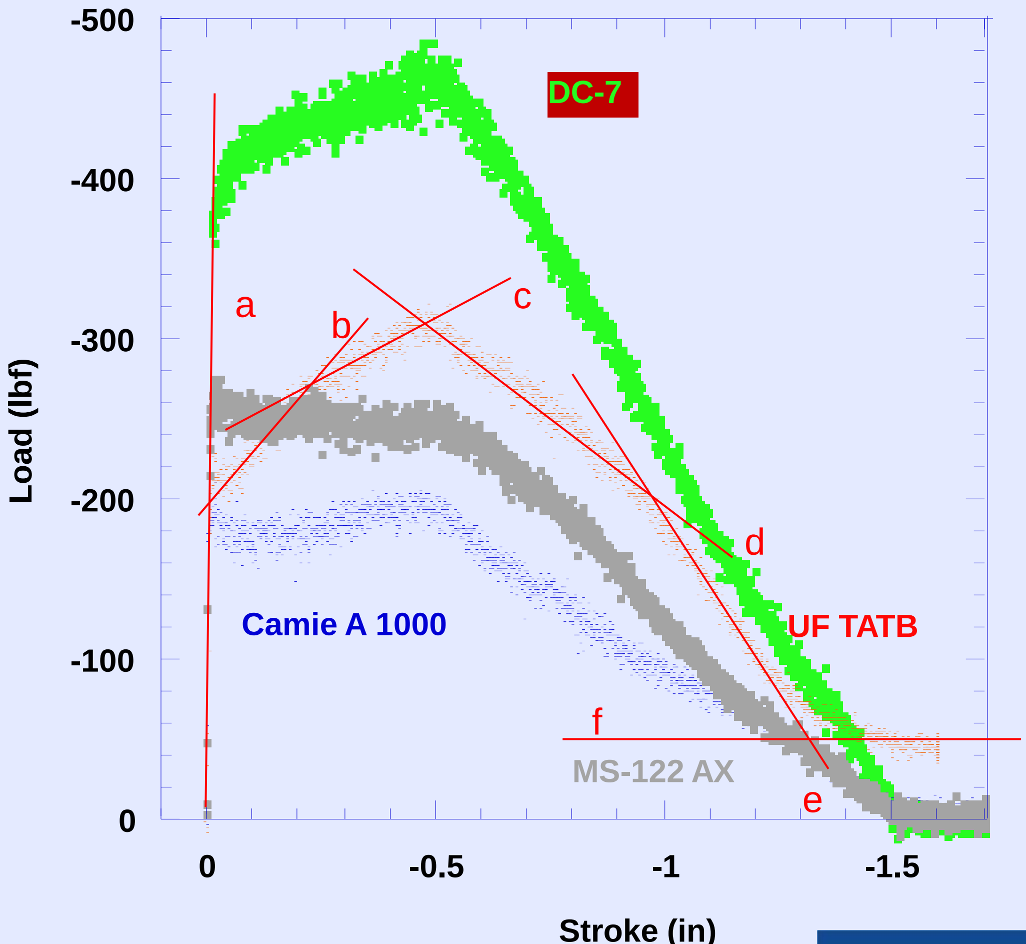
# Extraction force was different for various mold releases

1. FC wax required ~240 or 180 lbf to extract UF TATB
   - Shape suggests constant C of F
2. Silicone grease (DC-7) was less effective (400-480 lbf).
   a. Rapid increase
   b. Moderate increase

3. As part exits die $F_e$ decreased to zero except for UF TATB




*Fluorocarbon waxes reduced extraction force while one silicone increased it*

# Conclusions:

- Compression molded TATB compaction plots from one lot looked nearly the same independent of mold release agent used
- Models
  - Neither density-time nor Stress (Pressure) strain plots could ID MR improvement
  - Neither Bal'shin-Walker nor Kawakita were able to distinguish different Mold release effectiveness
  - Heckle plots differentiated various mold releases, but values didn't correlate with extraction data or density of part
- Maximum extraction force varied between 200-500 lbf depending on which mold release was applied
  - Extraction curves varied with mold release
  - Extraction almost always was not simple a function of friction between the UF TATB and the die.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# Backup SLIDES


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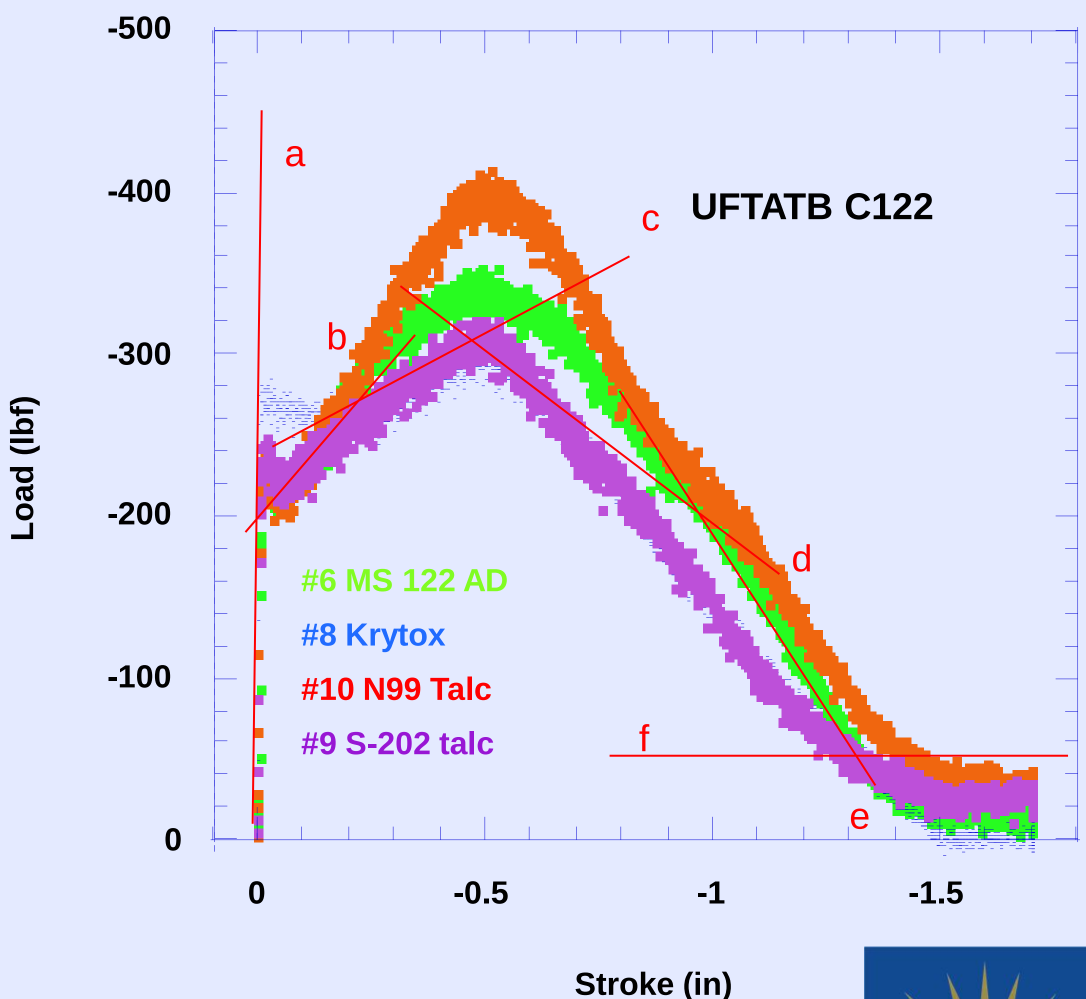
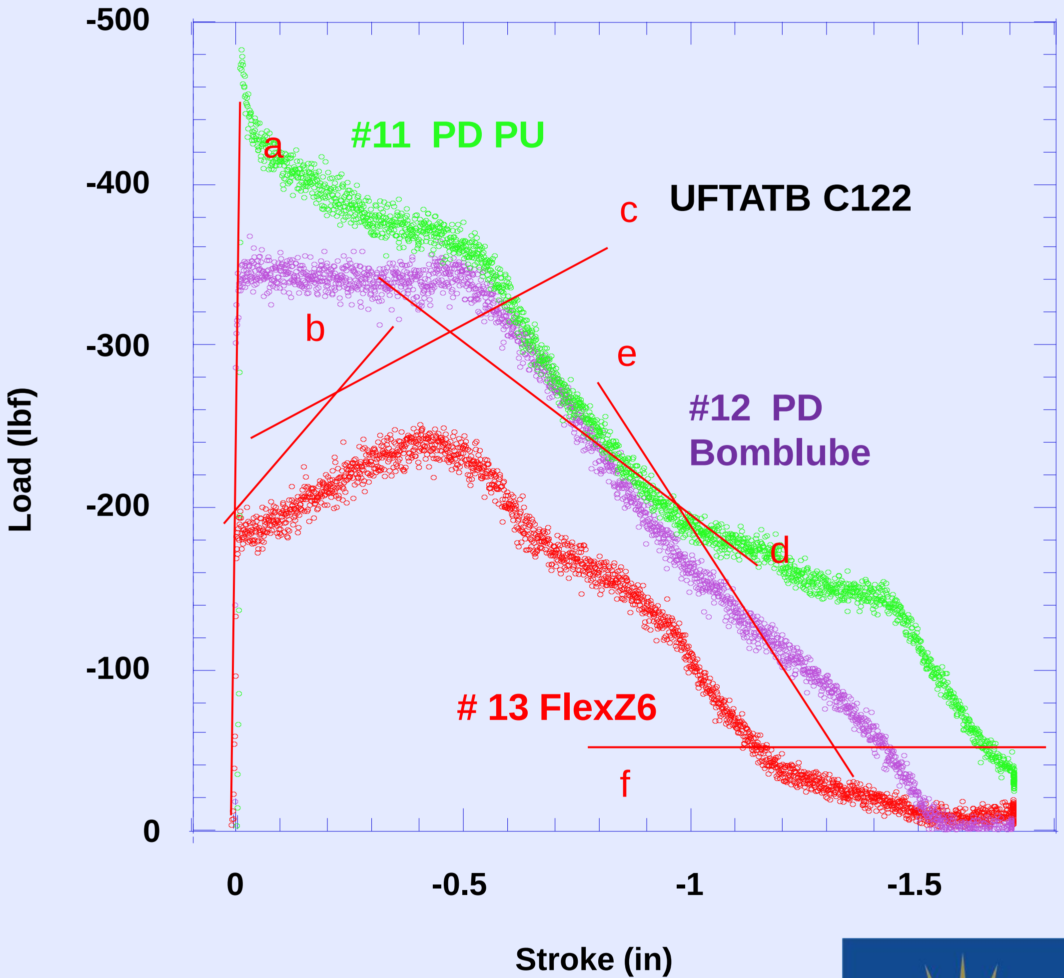
# Extraction characteristics for NMR and 4 mold releases were very similar

- Talc, Krytox and one of the MS fluorocarbon release agents showed remarkably similar release behavior
- Slopes after the part exits the die are fairly constant for these mold release agents
- All show a peak in the extraction force when the part exits the die

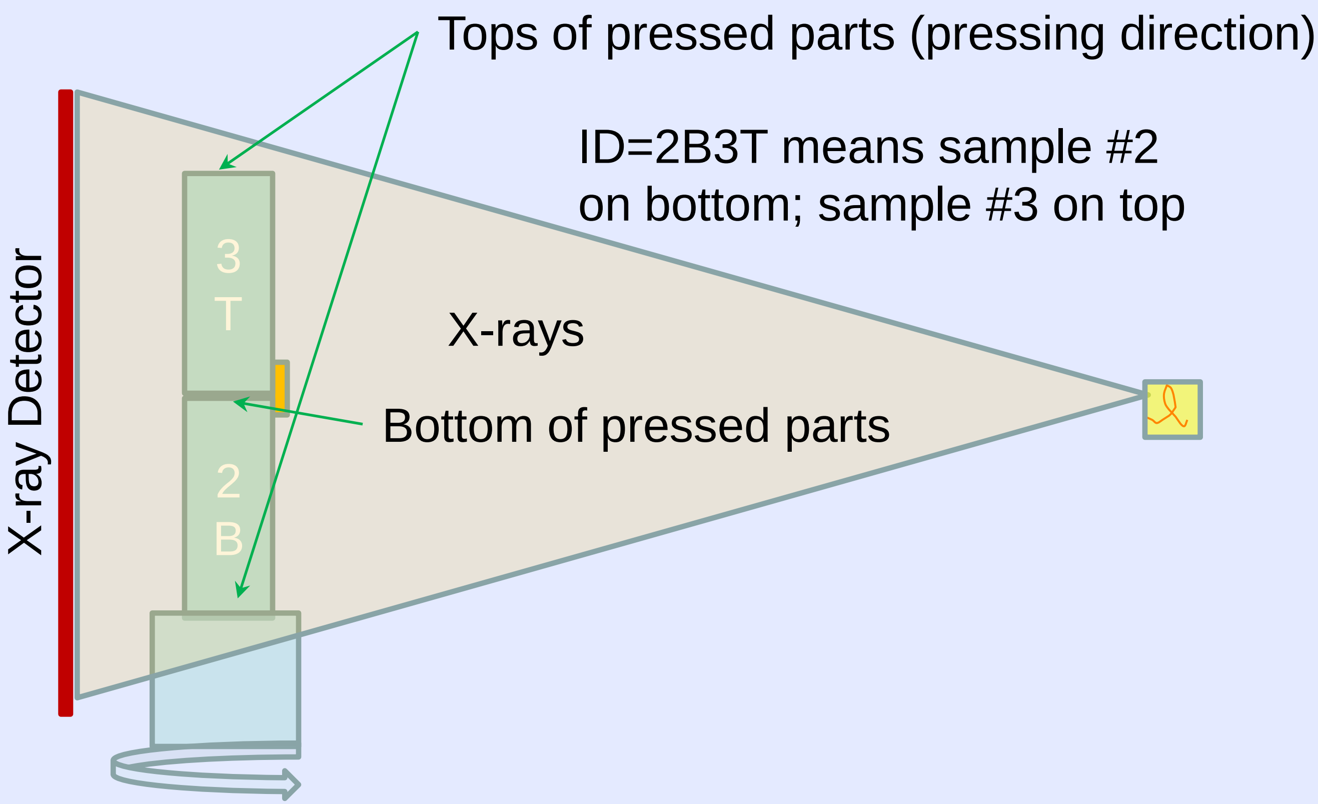


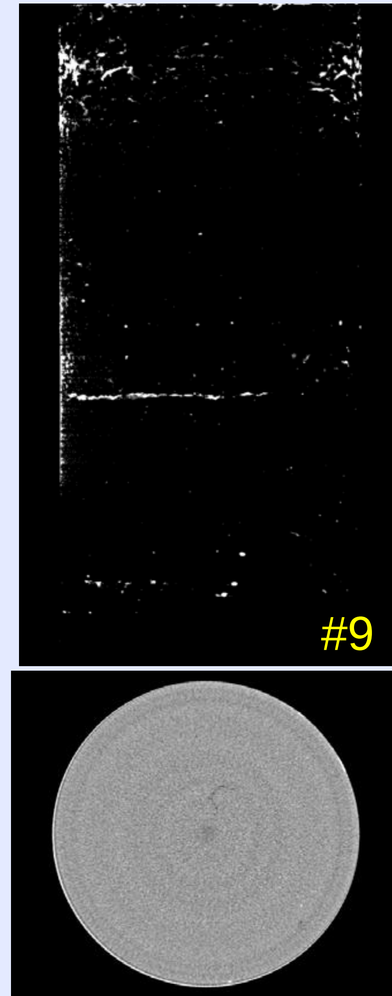
# PD PU, specially designed as a Urethanes, showed the most unusual extraction characteristics

- Flex Z 6 was a 3 step process that worked well but had an unusual extraction plot and low density UF TATB part
- Bomb lube (silicone) has been used in HE release agent for many formulations, but for UF TATB it's worse than no release agent.



# Xray CT setup ran 2 samples at a time




X-ray CT showed spherical talc MR incorporated in the UF TATB surface  but failed to show any density variation along the pressing direction



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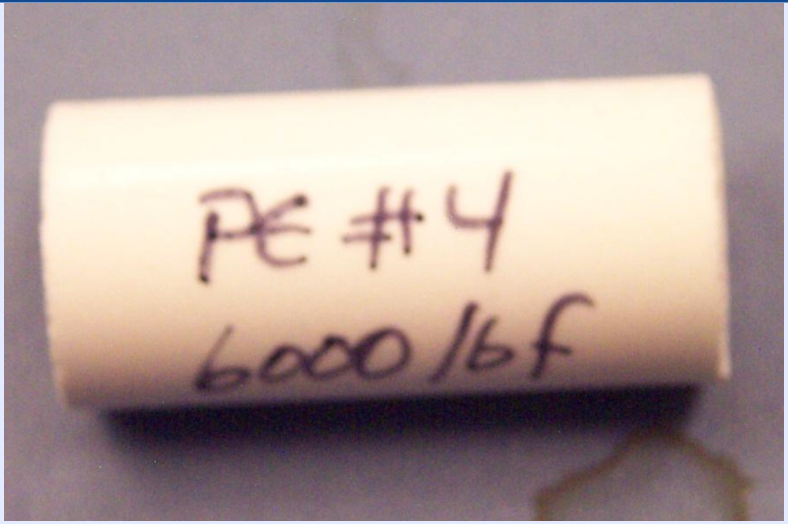
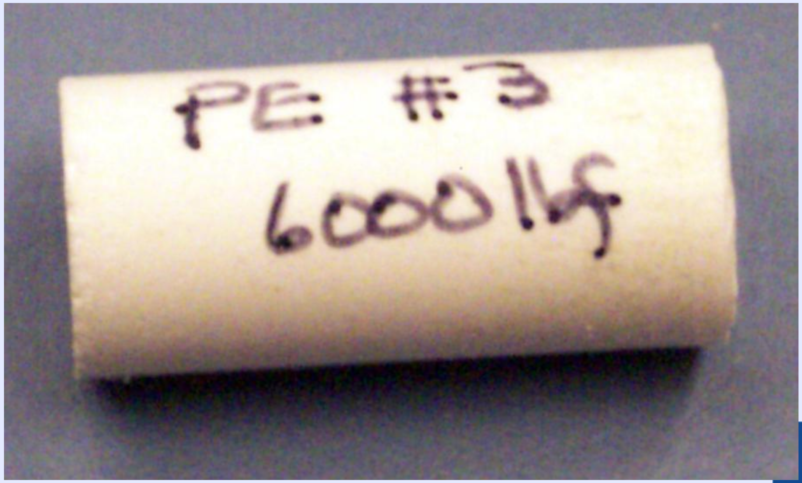
# Even with mold release PE "capped" on extraction





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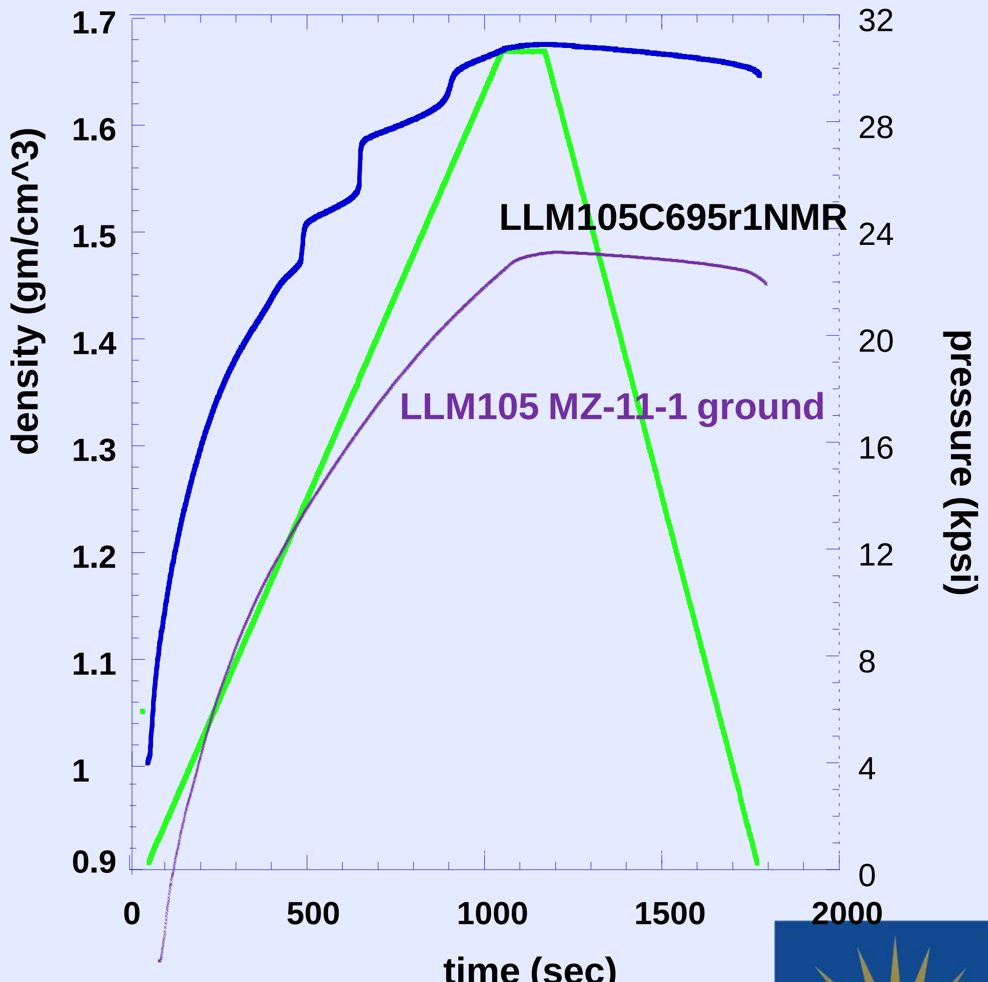
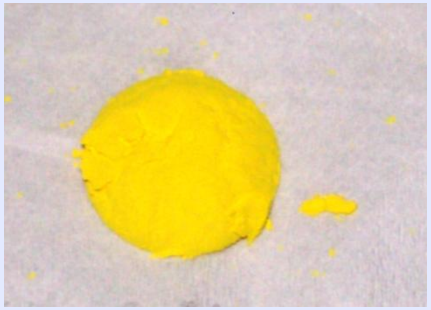
# Preliminary compression molding characteristics of LLM-105 powder at ~ 30 kpsi showed "caping"

1. Coarse (DMP process) & fine (ground) LLM105 samples were pressed from bulk density of about 1 and 0.8 to 1.674 and 1.477 gm/cc without MR
2. During lower plunger removal, fine LLM-105 produced the cap shown below



*An extraction program for the MTS was also written*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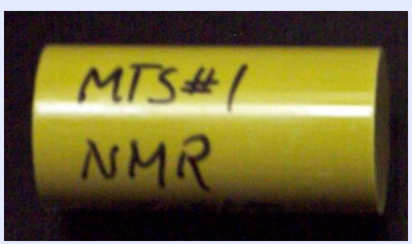
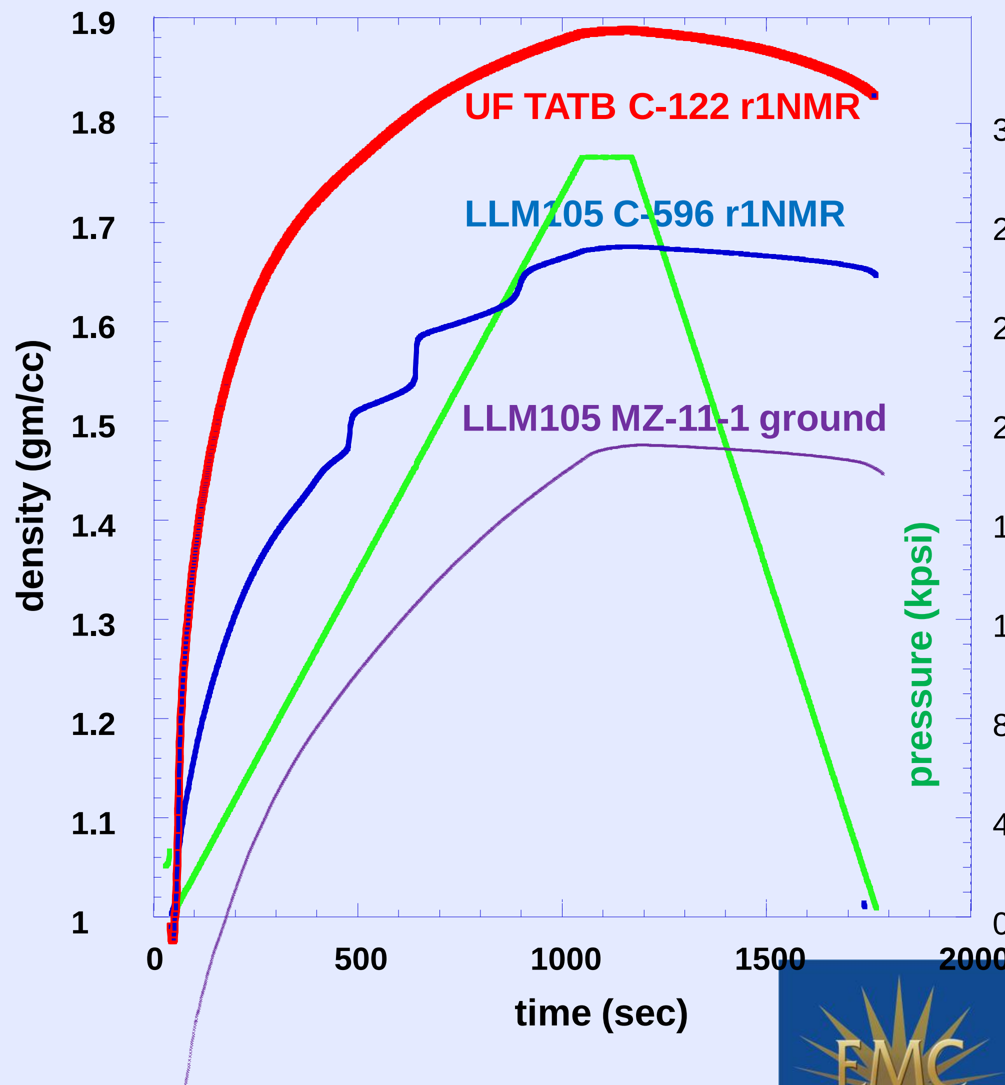
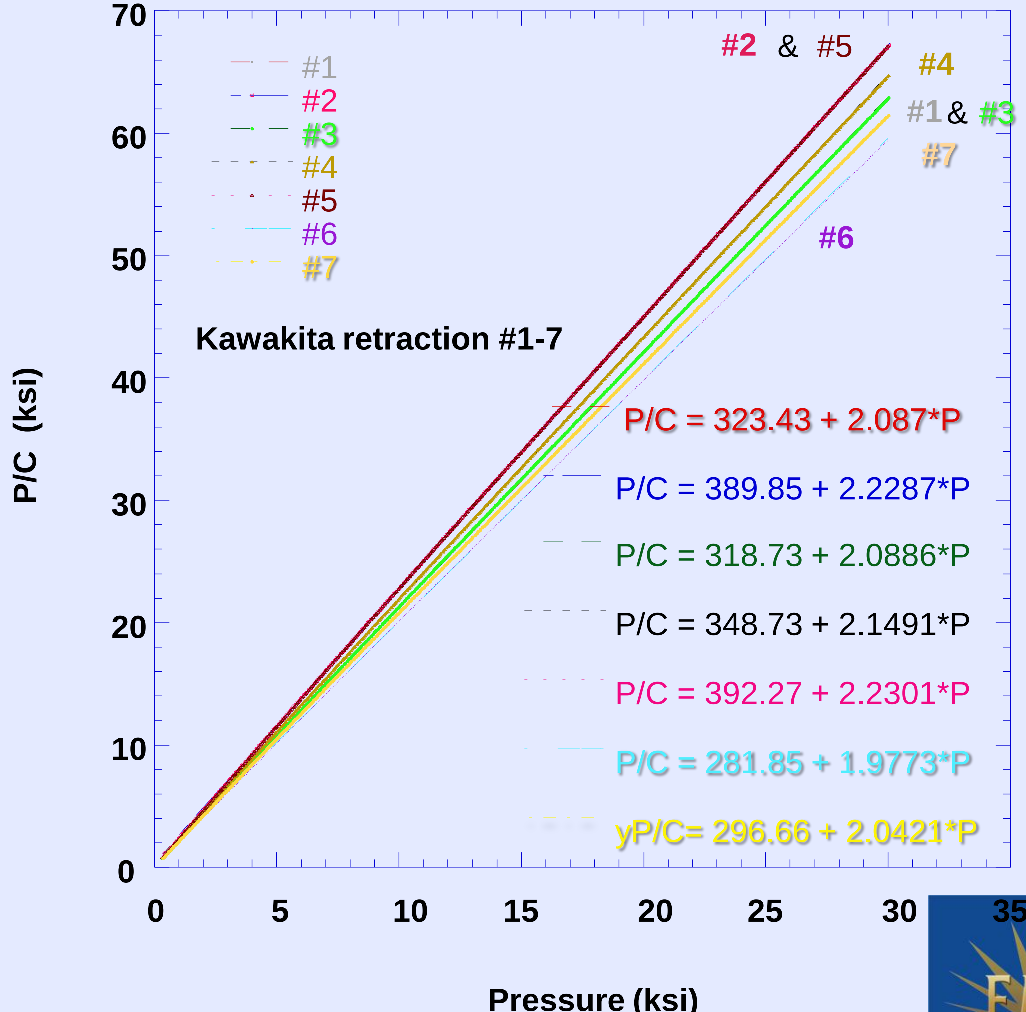
# UF TATB pressed to 1.900 gm/cc at ~ 30 ksi w/o MR but spring-back reduced the part density to 1.834

1. Precompressed to about 0.9 gm/cc
2. ~ 30 ksi gave 1.900 gm/cc max density
3. On release spring-back reduced the density to 1.833 gm/cc (possibly more).
4. Reasonable part recovered –measured density 1.8376 gm/cc



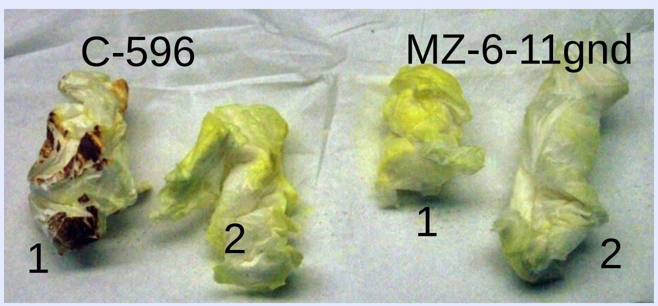



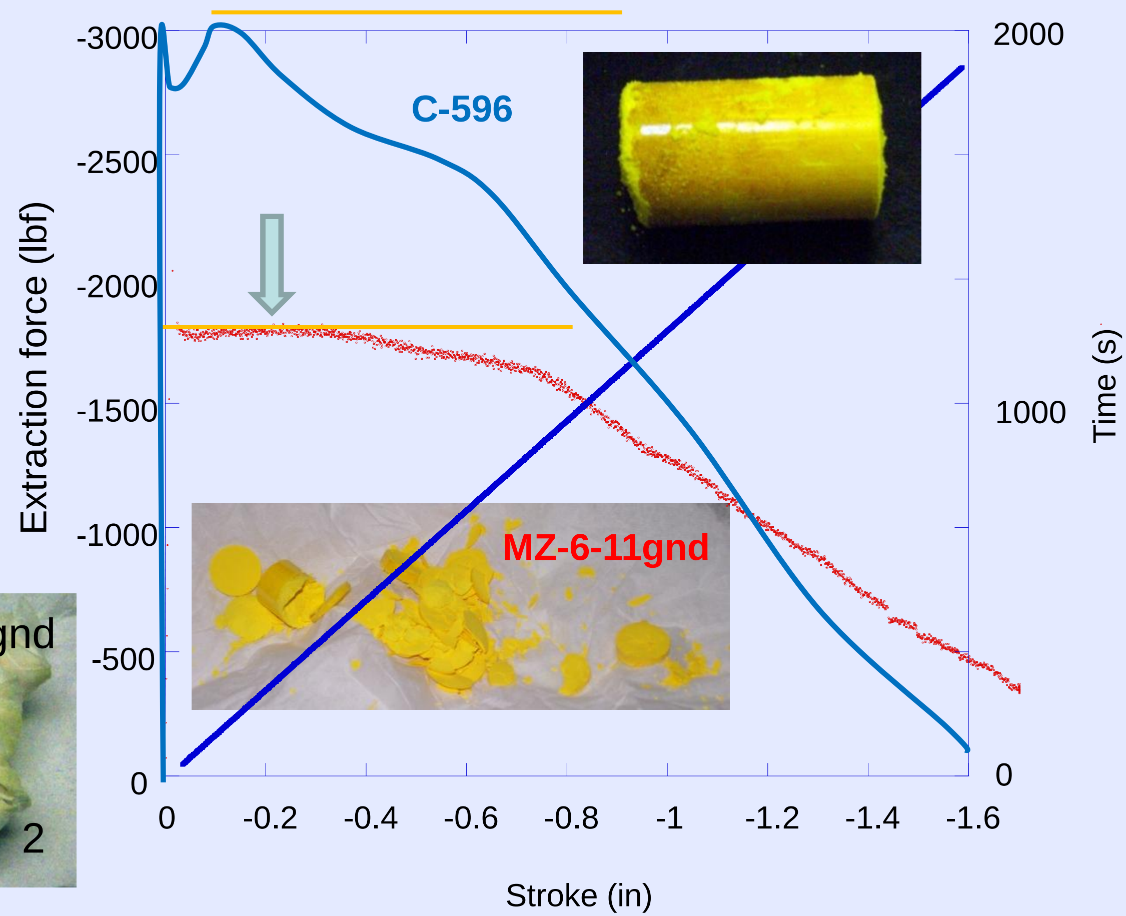
# Kawakita plots for the retraction portion of the pressing curve had intercepts of 300-400 psi (2-3 Mpa)



# LLM-105 required remarkable force (C-596→3530 and MZ-6-11-1→1867 lb-f) to extract parts

1. C-596 is the large IH batch which has a contaminant that attacked the die
2. MZ-6-11 (DMP process) ground ~6 μm to emulate UF TATB could not be extracted in one piece




*As might be expected, extraction characteristics of LLM-105 are very different from UF TATB*