RHEOLOGY: FROM HOMER AND HERACLITUS THROUGH GREEK (LIQUID) FIRE TO PROBLEM SOLVING IN THE POLYMER PROCESSING INDUSTRY

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HERACLITUS 6th Century B.C.

- Π Α Ν Τ Α Ρ Ε Ι
- EVERYTHING FLOWS
- ALLES FLIEßT
- TOUT S'ECOULE
- TODO FLUYE
- TUDO FLUI
- TUTTO SCORRE

See A.N. Beris and A.J. Giacomin " πάντα ῥεῖ : Everything Flows" APPLIED RHEOLOGY (in press)

Rheological concepts were understood before Heraclitus: S.A. Paipetis "The Unknown Technology in Homer", Springer (2010) refers to a single verse in ODYSSEY 4.42 (8th century BC)

ἅρματα δ' εκλιναν προς ενώπια παμφανόωντα

(they) leaned the chariots against the gleaming entrance wall

The same verse also appears in ILIAD 8.435 (8th Century B.C.)

GREEKS were aware of CREEP of the wooden wheels and axle of chariots under prolonged loading, in HOMER's time (8th Century B.C.)

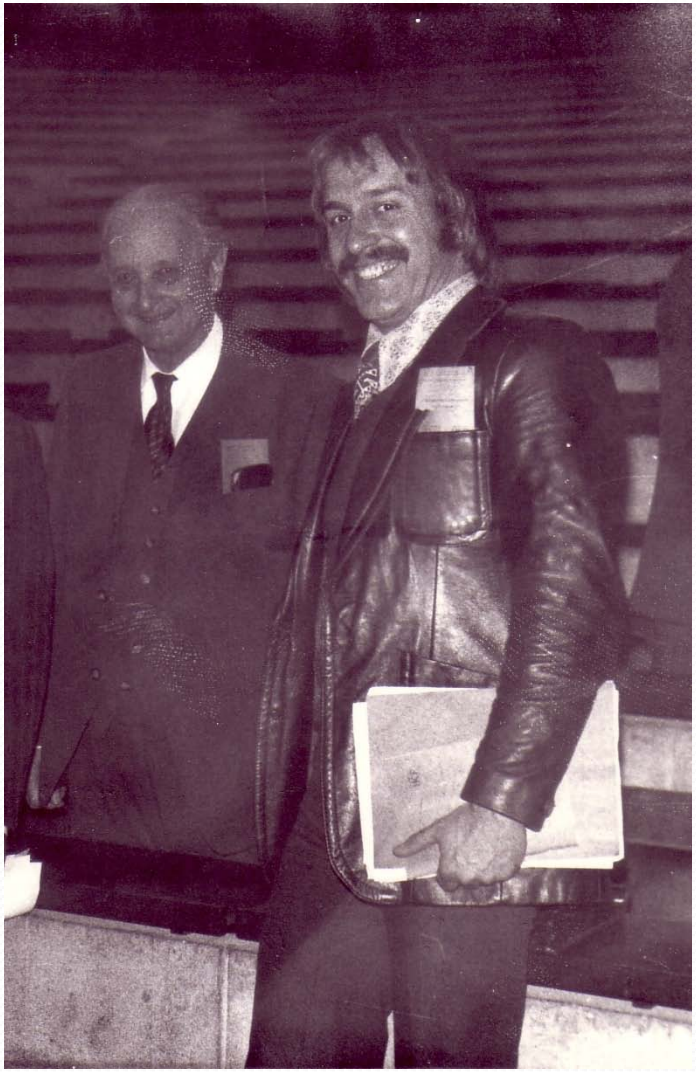
The Byzantines of Constantinople (who called themselves Ρωμαῖοι (Romans)) used "fire ships" equipped with "siphons" starting in 671 AD. The invention is credited to Kallinikos (a Greek) from Heliopolis, Syria (ὑγρόν πῦρ (liquid fire))

For a detailed account: J.R. Partington "A History of Greek Fire and Gunpowder" Johns Hopkins University Press (1999).

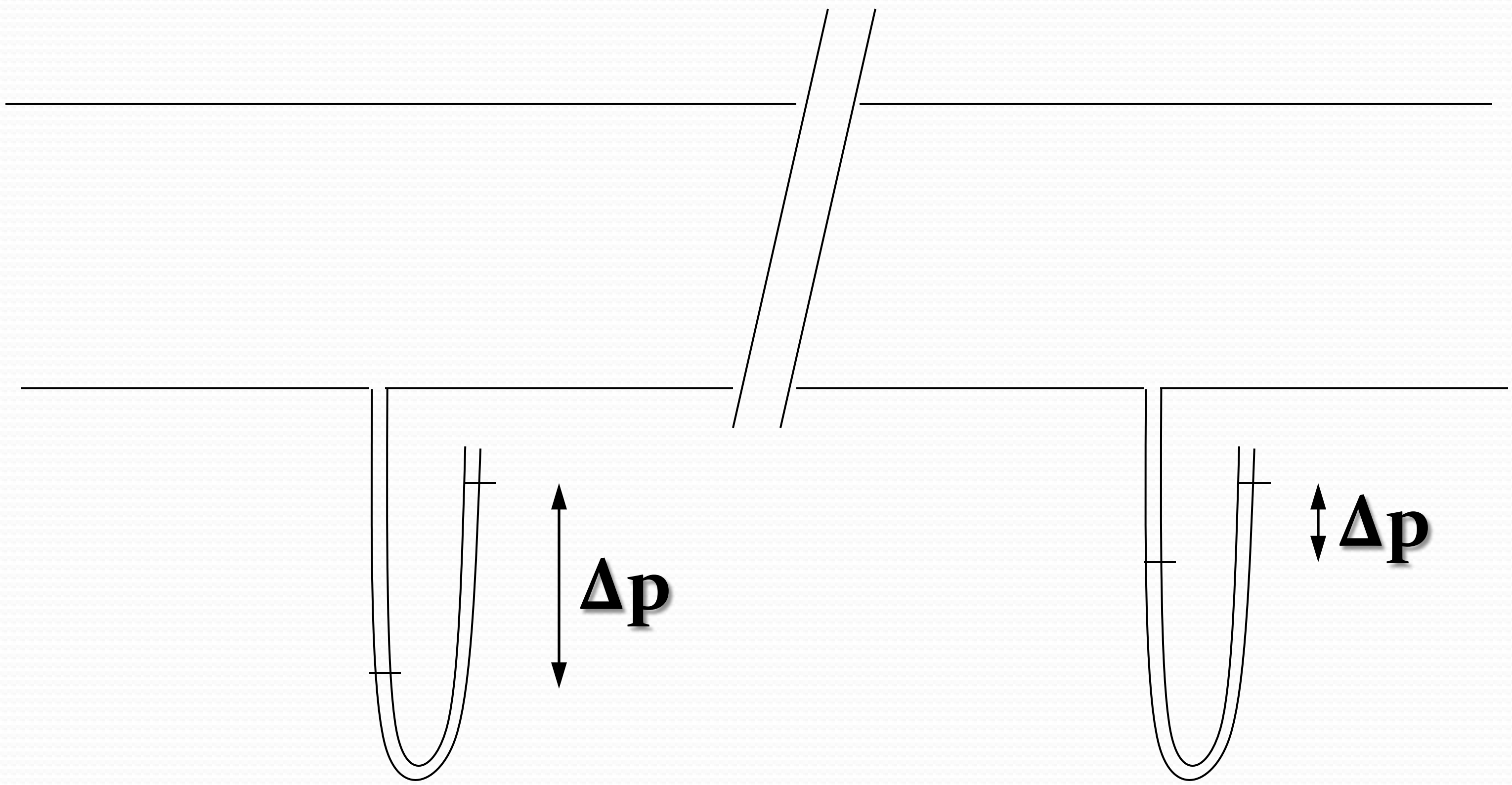
- **KALLINIKOS and his craftsmen must have faced some formidable rheological problems, similar to those investigated by KARL WEISSENBERG (1893-1976) during World War II, in Britain, on flame-thrower materials (discovery of normal stresses).**

- **VISCOSITY, ELASTICITY and YIELD STRESS must have played very important roles in PUMPING and in the CONTROL of FLASHING and SPREADING tendencies of the LIQUID coming out of the "siphon" (probably a GEL of a thickened fuel, like NAPALM?).**

Karl Weissenberg
and
John Vlachopoulos
U. Stuttgart (February 1975)



Robert J. Arnzen's (Doctoral Candidate in Mech. Eng. 1965-1968) water-tunnel and manometers at WASHINGTON UNIVERSITY, ST. LOUIS, MO



Pressures measured were different after the addition of a very small amount of a bright blue dye in the water

ARTHUR S. LODGE visited Washington U. for a seminar presentation (1966) and immediately explained the phenomenon. The bright blue dye was a polymer. The pressure differences (between water-only and water-plus-dye) were due to bending of the streamlines (hole pressure error*)

*** Lodge and co-workers, NATURE, <u>217</u>, 55-56 (1968)**

PROBLEM SOLVING IN THE POLYMER PROCESSING INDUSTRY USING:

- ❑ **RHEOLOGICAL MEASUREMENTS**

- ❑ **COMPUTER FLOW ANALYSIS (UNI-DIR, 2D, 3D)**

THE PLAYERS:

- **RESIN PRODUCERS (large chemical companies like BASF, DOW, DUPONT, EXXONMOBIL, LYONDELLBASELL..)**

- **MACHINE MANUFACTURERS**

- **PROCESSORS (about 100,000 around the world, with annual sales ranging from $500K to a couple of Billion Dollars)**

The vast majority of processors rely on technology supplied by the Resin Producers and Machine Manufacturers

In industry consulting, Freeman Dyson's quote is meaningful:

“ A good scientist is a person with original ideas. A good engineer is a person who makes a design that works with as few original ideas as possible. There are no prima donnas in engineering.”

Freeman Dyson a physicist, born in 1923, had a very illustrious career.

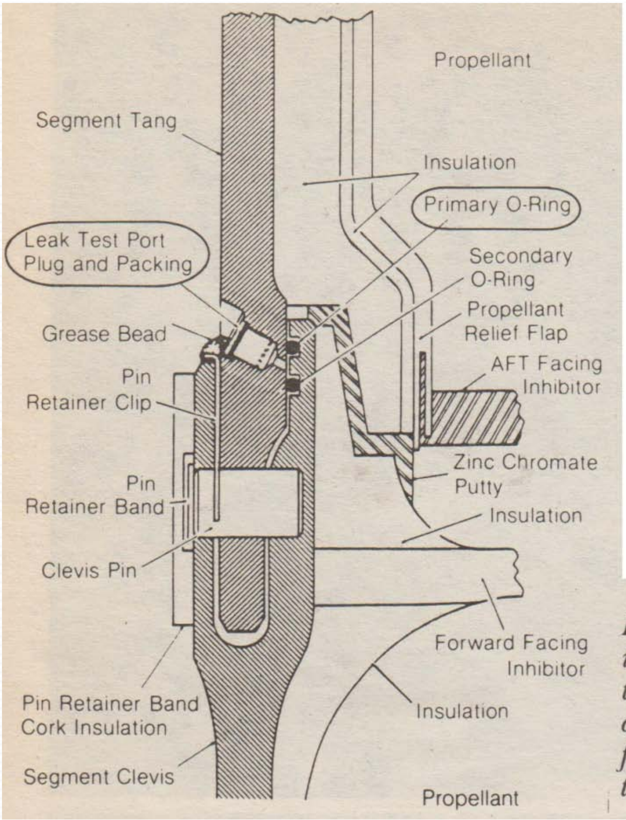


FIGURE 13. An incorrectly sealed leak test port could provide an escape route for a flame which burns past the primary O-ring.

- **Incorrect sealing was the root cause of the space shuttle CHALLENGER accident**
- **Guess how was this discovered!**

One of the best known physics celebrities of all time, carrying out one of the simplest rheological experiments:

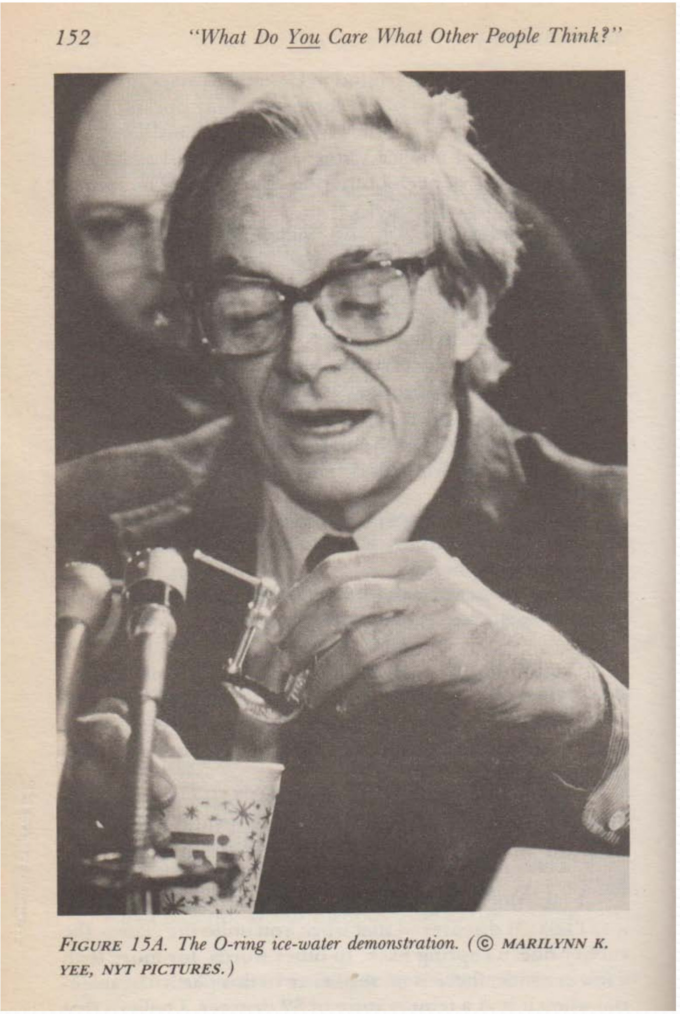

152 "What Do You Care What Other People Think?"

FIGURE 15A. The O-ring ice-water demonstration. (© MARILYNN K. YEE, NYT PICTURES.)

Bantam Press (1988)

<u>RICHARD FEYNMAN</u>, member of the Presidential commission investigating the space shuttle CHALLENGER accident (1986) (O-ring rubber):

"Finally, when I get my ice water, I don't drink it! I squeeze the rubber in the C-clamp, and put them in the glass of ice-water……..there is no resilience in this particular material when it is at a temperature of 32^{o}F."

I have no picture with Feynman, but with another physics celebrity

John Vlachopoulos and Werner Heisenberg (Pnyx, Athens, June 3, 1964)

ONE OF MY PROBLEMS: INJECTION MOLDING (I.M.) OF TWIST-OFF CAPS

It was impossible to mold twist-off caps with a new PE grade, at a large corporation

The I.M. gate is on top (inside) and the <u>polymer must flow through the tiny "bridges" to form the bottom ring</u>.

GLOBAL PRODUCTION OF SYNTHETIC POLYMERS

1 MILLION TONS in 1945

300 MILLION TONS (est) in 2015

At $2000 on average per ton plus using James Throne's rule of 2 for processing, we end –up with

$1.2 TRILLION global business

The twist –off cap business is over $3 Billion annually

- The wall shear rate in the “bridges” was calculated at about 100,000 s^{-1} and strong WALL SLIP was suspected.

- From the two resins examined, the “good” resin had a much higher wall slip velocity (as measured by the Mooney method (developed in 1932)).

- The “bad” resin was subsequently modified by my customer to match the wall slip characteristics of the “good” resin.

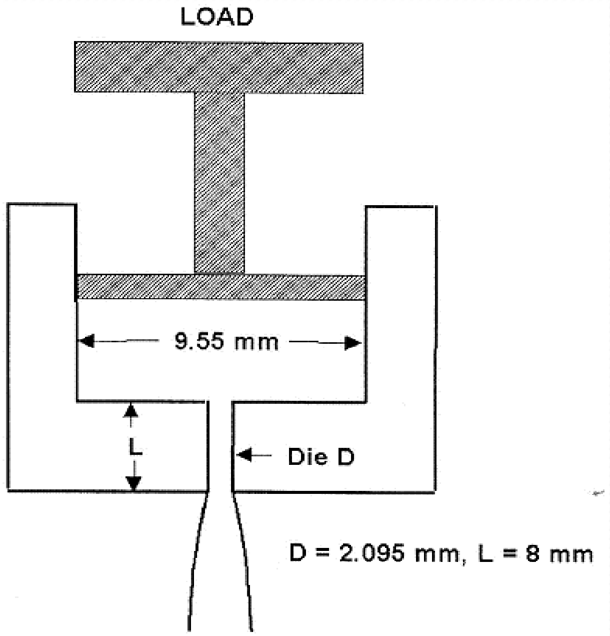
- Twist-off caps were injection molded using the modified resin, without further problems.

Material data sheets provide just one (and a very low-tech) rheological property

MELT INDEX
(ASTM D1238)

MELT INDEX (MI → grams in 10 minutes)
STANDARD LOAD 2.16 kg, Standard temperature (190°C for PE, 230°C for PP, called Melt Flow Rate).

$$\dot{\gamma} = \frac{1838}{density} \times \left(MI \ \ value \right)$$



Schematic of a melt indexer

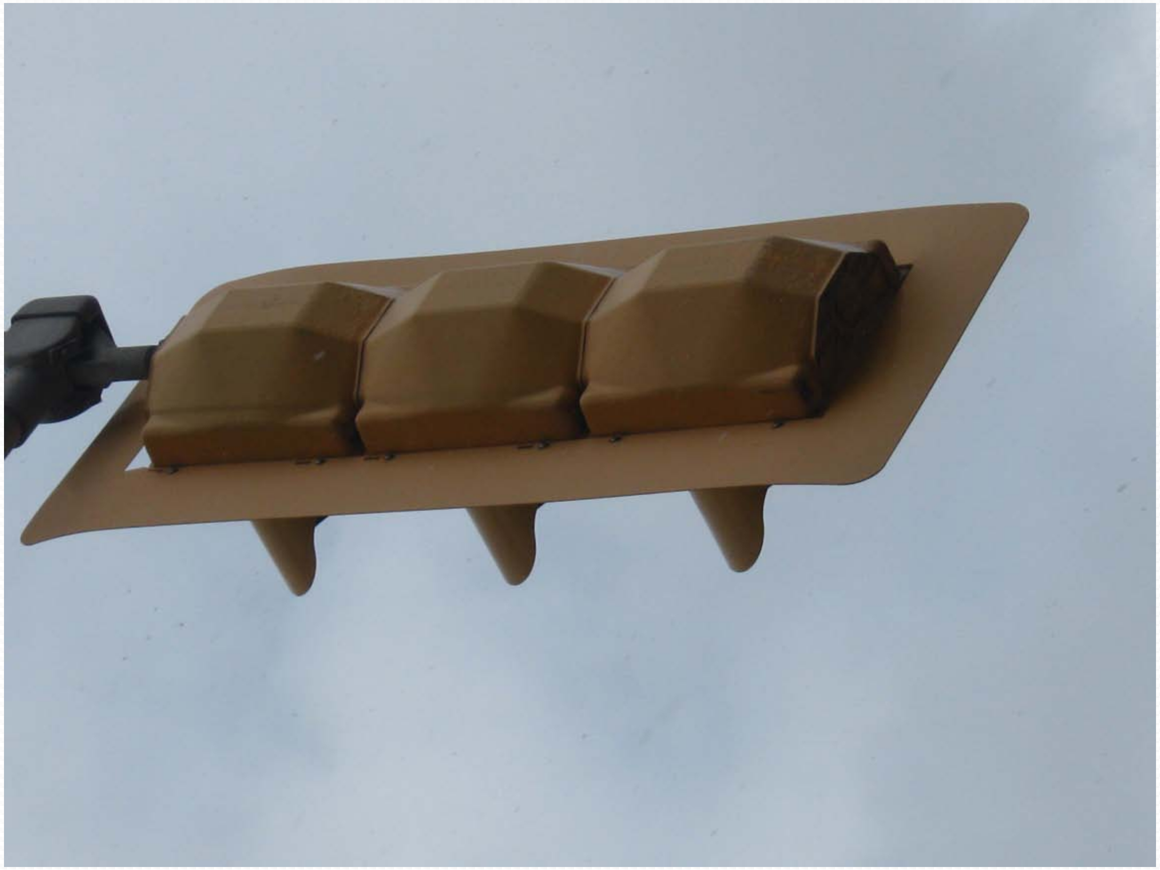
For a "typical" PE:

$$\dot{\gamma} = \frac{1838}{766} \times MI = 2.4 \times MI$$

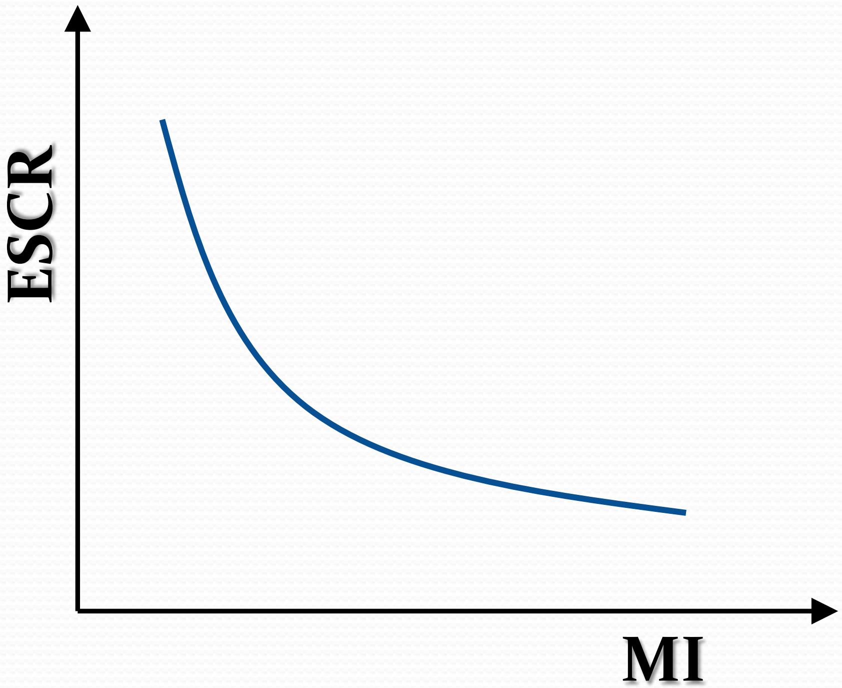
$$\tau_w = 1.94 \times 10^4 \ \ Pa$$

HIGH LOAD Melt Index (HLMI) is usually with 21.6 kg (sometimes with 10 kg or 5 kg).

PROBLEM: **Cracking and structural integrity deterioration was noted in traffic light housings in Canada (injection molded Polycarbonate (PC))**



Environmental Stress Cracking Resistance (*ESCR*) varies with *MI* (*MW*)

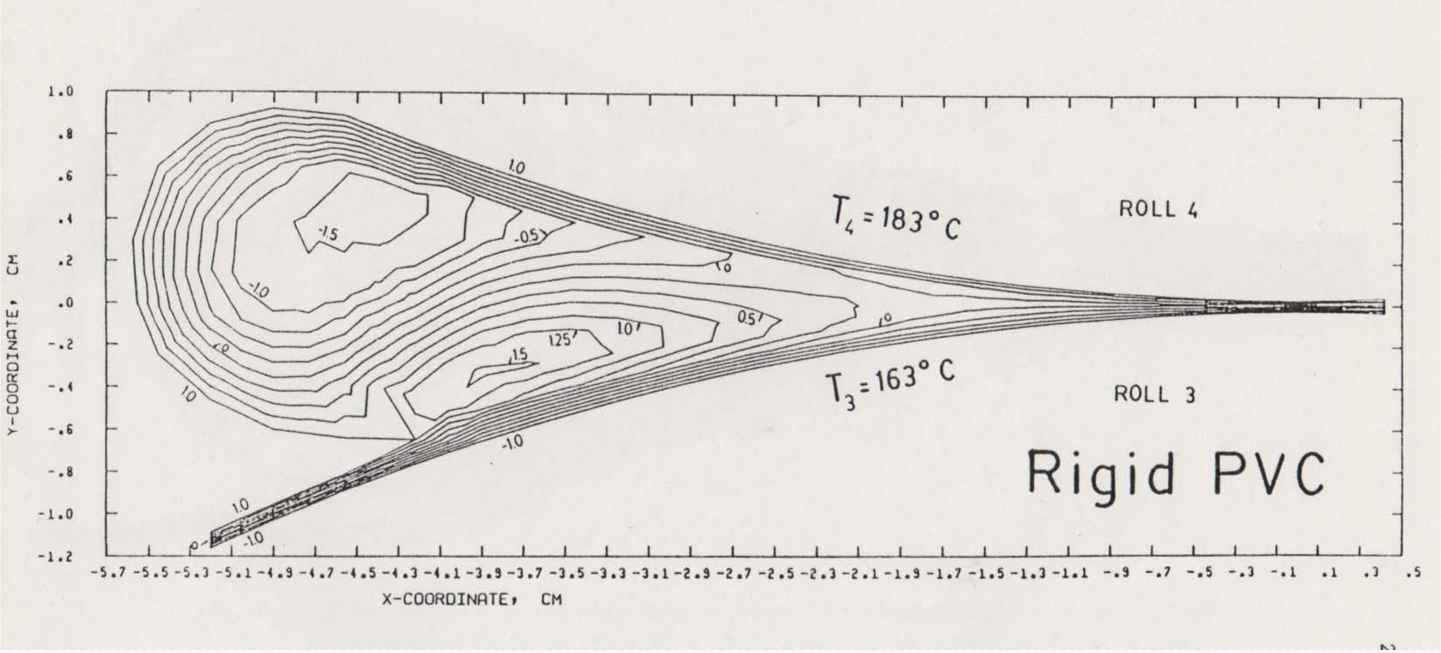


SOLUTION: *MI* less than 12 → No *ESC*
MI* between 12–18 → sometimes *ESC
MI* more than 18 → always *ESC
(For the traffic lights PC housings)

PROBLEM: Calendered thick PMMA sheet installed in trains in the US, made people dizzy at night!

Customer observed that there was a large amplitude waviness in the sheet, and believed that it was due to entrance flow instabilities during calendering.

Customer had seen publications/ presentations by E. Mitsoulis, F. Mirza and J. Vlachopoulos



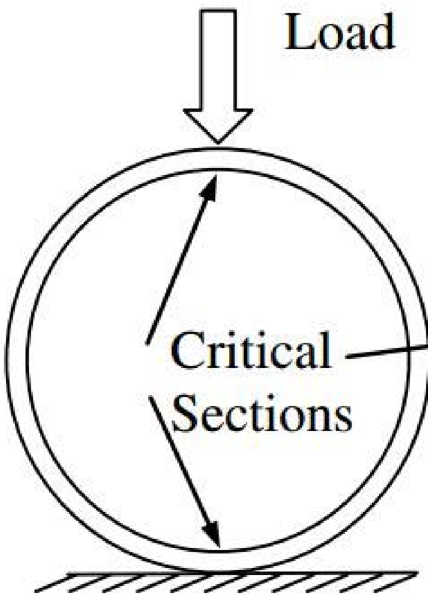
Polym. Eng. Sci., 25, 6-18 (1985)

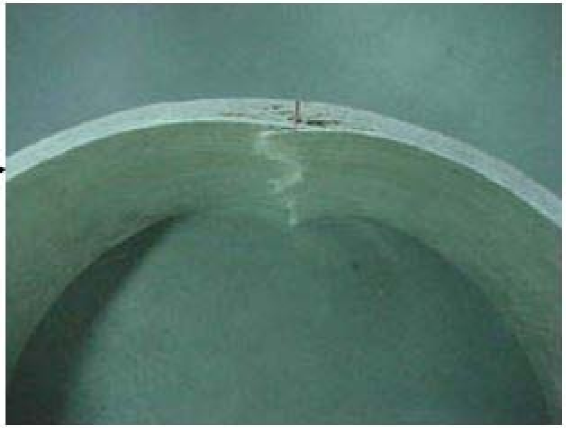
- **Computer simulations by Evan Mitsoulis, showed that there were NO VORTICES for the customer's operating geometry, conditions and material (entry was too close to the nip, no melt bank).**
- **The large amplitude surface waviness seemed to correlate to the frequency oscillations of the rotating cylinders.**
- **NEXT QUESTION: How come, when we calender the competitor's resin on our machine and install it in train windows, passengers do not get dizzy? (under identical operating conditions)**

- Company chemists believed that the competitor's PMMA resin and their PMMA resin were "virtually identical" in molecular architecture and molecular weight distribution.

- First normal stress measurements (by cone-and-plate) proved that the competitor's resin was more elastic (hard to detect high molecular weight tail).

PROBLEM: Extruded large diameter pipes tend to fail the parallel plate loading test when filled with $CaCO_3$





Picture from: R.M. Guedes, Comp. Struct., 88, 188 (2008).

- **$CaCO_3$ is used as a filler to reduce cost.**
- **Frequently, the extrusion equipment does not have adequate extensional flow regions, necessary for good distributive and dispersive mixing.**
- **Even with good mixing, heavy $CaCO_3$ loadings result in significant increase in viscosity, increase in stiffness (modulus) and decrease in failure strain.**

The well known equations for spheres:

- **Einstein-Bachelor (viscosity):**

$$\eta_c = \eta_p\left(1 + 2.5\phi + 6.25\phi^2\right)$$

- **Einstein-Guth-Gold (modulus):**

$$E_c = E_p\left(1 + 2.5\phi + 14.1\phi^2\right)$$

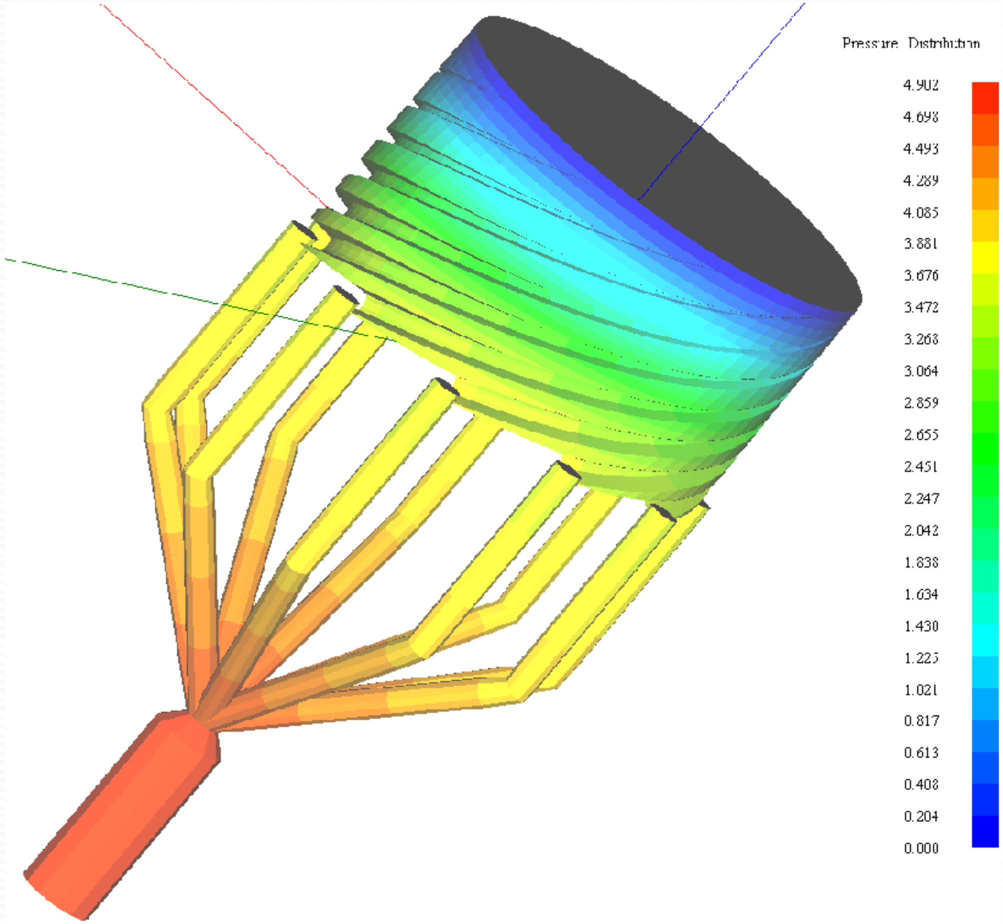
- **Failure strain:**

$$\varepsilon_c = \varepsilon_p(1 - 1.105\phi^{1/3})$$

give (surprisingly) satisfactory approximations, even outside the intended regions of validity in volume fraction ϕ.

FLOW ANALYSIS is an excellent tool for die design and troubleshooting

PRESSURE FIELD IN A SPIRAL DIE



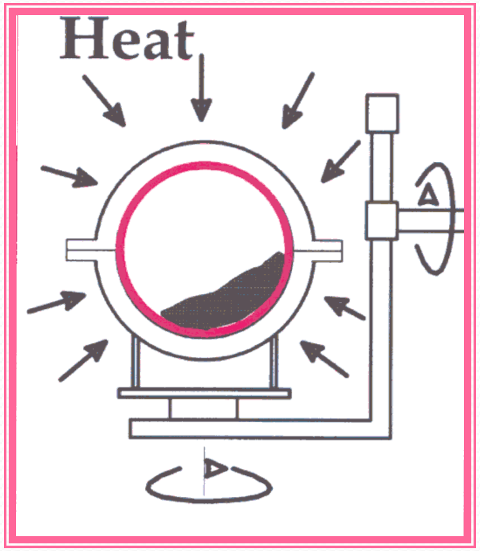
J. Vlachopoulos, R. Castillo, N. Polychronopoulos and S. Tanifuji "Blown Film Dies" chapter in "Design of Extrusion Forming Tools" Eds. Olga S. Carneiro and J. Miguel Nobrega, Smithers Rapra, UK, 2012

- **Most problems are <u>NOT</u> associated with the high shear stress at die lips (SHARKSKIN/MELT FRACTURE,……..hundreds if not thousands of publications)**

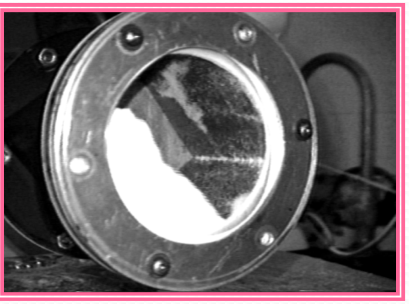
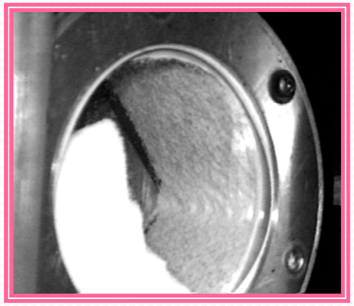
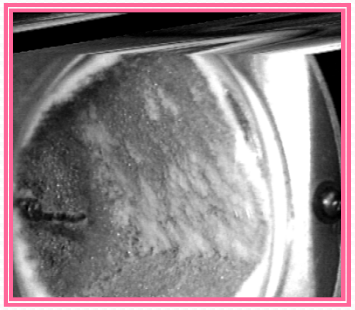
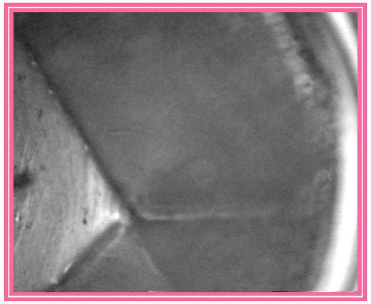
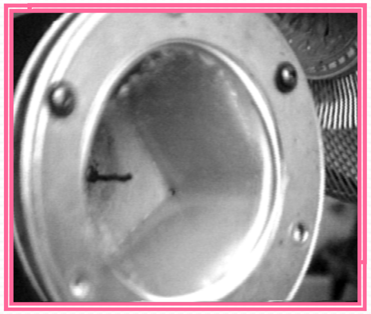
BUT, with the LOW SHEAR RATE regions inside the die channels.

- **Prolonged operation with wall shear rate regions of less than 10 s^{-1} results in black spots and/or deterioration of the optical clarity of extruded film (no publication by anyone….but pending).**

PROBLEM: Is it possible to determine rotomoldability of resins in the laboratory?



Virtually zero $\dot{\gamma}, P$

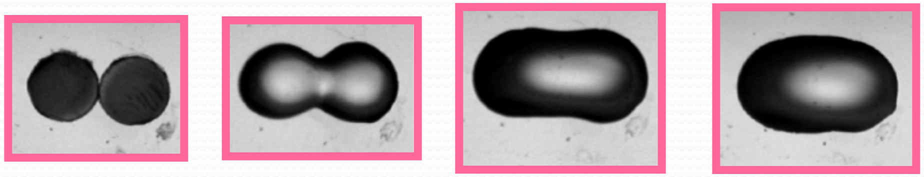
Induction	Adherence	Coalescence	Densification	Cooling
				

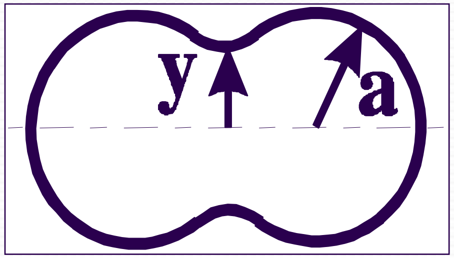
Coalescence of particles

❑ Growth of neck, at high temperatures under the microscope (VERY USEFUL DEVICE)

1. Frenkel's model (applicable for the start), was extended to completion.
2. Elastic effects added in new model.
3. Zero shear viscosity, G' and surface tension determine ROTOMOLDABILITY.

t=0 sec t=135 sec t=270 sec t=390 sec





$$\frac{Y}{a} = \left(\frac{\Gamma t}{\eta a_o} \right)^{1/2}$$

Frenkel's model

SOME CURIOUS PROJECTS:

BI-AXIAL orientation of SAUSAGE CASINGS (imagine film blowing of 2-4 cm diameter tube with some ……..confidential details).

❖CALENDERING of bread dough for the production of CRACKERS (surprisingly good predictions using power-law viscosity model).

❖ EXTRUSION of BREAKFAST CEREAL , in the shape of dinosaurs (long necks required computer flow analysis of profile die).

❖ The dentist who built a capillary viscometer (1.4 mm diameter), for assessing DENTAL FILLING MATERIALS (ought to know that extrusion force is due to capillary plus entrance flow resistance).

**RHEOLOGY
IS A VERY USEFUL
AND
POWERFUL TOOL
FOR PROBLEM SOLVING
IN
INDUSTRY**

I thank my students and co-workers, in particular:

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THANK YOU

Q & A