

COMPPRO: Constitutive Equations and Solvers International Workshop  
19 January 2001, University of Bradford, UK

**Some Outcomes:**

Prepared by Phil Coates (so any misunderstandings are my fault!)

[ ] = comments added to my original draft

**Some Global Points** (mainly from a discussion session at the end of the day)

1. Thermodynamics must be incorporated (c.f. Ottinger) into constitutive equations (CE's) re dissipation, strain rate effects
2. We should recognise that different CE's aim at some different goals and some common goals, e.g. it is possible to take a view (simplistically) that integral equations based on modified KBKZ/ Wagner etc emerged in the rheology area, with the primary aim of process flow predictions, but with aspects which refer back to molecular features; the 'pom=pom' approach was more concerned with representing molecular-related issues, going on to fit observed rheology and then make process flow predictions.

*schematically:*



3. Physicists and engineers may have different requirements – processors need to simulate process flows as accurately (and often as quickly) as possible without necessarily developing molecular feature understanding; physicists/chemists need to develop understanding, which may be relevant to polymer design. Another way of expressing this is that rheology features can be used to build CE's which can then be used in processing predictions, requiring little molecular feature understanding; molecular topology issues aim to clarify understanding of materials, not necessarily (but also not excluded from) providing better process modelling.
4. So far, all of our CE's are still essentially continuum mechanics approaches, dealing with volumes of polymer which contain large numbers of molecules – ensemble averaging – certainly not atomistic/ individual molecule levels.
5. Some comments on CE progress in past decades
  - A key improvement is the use of the orientation tensor (physics!)
  - Previous problems with Planar flows have been overcome (it is recognised that the integral equation alone is not enough)
  - An issue: - is chain stretch to be treated as local or not [relative or absolute]? – if local, it depends on history and needs to be under the CE integral part
  - Possibly 2 constants are sufficient for a working CE (integral)? It is desirable to describe extension and shear flows with a minimal number of non-linear parameters.
6. Increased experimental information, in addition to standard shear and extensional rheology, is important – e.g. scattering, dielectric spectra. Not required for homogeneous melts? – but is for CE's
7. New possible standard materials need to be defined, in addition to IUPAC materials, for CE comparisons, because of advances, e.g. in metallocenes for tailoring of polymers
8. Benchmark flow solutions are also required, with clear information available from each CE/ solver route.
9. Possibly those describing current CE's are using different words to describe similar features? – is a 'mapping' of the maths of different CE approaches likely?

*Lateral thinking Question* – what is predicted by our current CE's which is not observed experimentally, but which might be? [One response: An example of observed in simulations phenomena that have not been observed yet experimentally (but which might be, especially with sophisticated multi-point temperature probes inside the die) are non-isothermal viscoelastic simulations with the K-BKZ model of extrudate swell from a planar die, where the phenomenon of bending of the extrudate occurs [see, Barakos, G., Mitsoulis, E., "Non-Isothermal Viscoelastic Simulations of Extrusion through Dies and Prediction of the Bending Phenomenon", J. Non-Newt. Fluid Mech., 62, 55-79 (1996). This also relates to comment .12 below. The same bending phenomenon has been predicted in coextrusion of polymer melts through slit dies, see Barakos, G., Mitsoulis, E., "Viscoelastic Simulations of Stratified Bicomponent Extrusion through Slit Dies", Intern. Polym. Proc., 11, 147-153 (1996)].

10. Global observation – all of the CE/solver workshop is geared to continuous processes (mainly extrusion), ignoring the major industry sector, injection moulding, where CE's are simplified, with solvers aimed at relatively rapid answers!!
11. Temperature effects (non-isothermal flow fields) have not been addressed here

### Some specific points/ questions raised:

#### *Around Wagner presentation*

1. Pom-pom used mean field re tube diameter – if squeeze tube (diameter falls) then strain energy is increased;
2. In pom-pom model, stretch is outside the integral, so if get hardening in planar 1 direction, will also get it in planar 2 direction;
3. Wagner MSF approach separates out orientation [, reversible] and irreversible components of flow
4. One non-linear parameter used for all extensional flows; a second parameter c.f. rotation (dissipative) effects – shear predictions now accurate.
5. What about a *gradual* transition in material grades, from linear to branched?
6. Many different types of long chain branched melts are now being developed, possibly leading to different behaviours from those modelled at present.
7. What is the behaviour of the integral model in extensional recovery experiments? (Answer – it has some irreversibility built in)
8. Fitting techniques used? Also, it would be nice to see steady state extension
9. Dissipation taken into account in Wagner – leads to clear turnover in stress growth curves when get equilibrium between stress work and dissipation ( $\dot{\gamma}^2 = 0$ )

#### *Around McLeish presentation*

1. Pom-pom approach is not simply aimed at LDPE flows, but at developing a predictive molecular theory for rheology of model architectures
2. Doi Edwards original paper (1978) did acknowledge problem of chain stretch
3. Convective constraint release (CCR) removes the unphysical stress maximum ( $\dot{\gamma}$  strain rate) predicted for pure reptation
4. CCR is a 'local process' – local treatment retains structural information (c.f. n scattering data for orientation)
5. The end of extensional hardening is real – a material parameter
6. Pom-pom approach does not necessarily require a very large number of parameters; key fitting variables are parameterisable by a few
7. Ideas of 'seniority' and 'priority' (how many arms connected to – limits extension) of molecular features found to be useful
8. Can't treat average generic molecules – backbones are very slow and outer parts very fast in relaxations – affects damping function
9. Molecular pattern changes with flow rates
10. Use of 'snipping' to remove fast relaxing outer layers from calculations – reduces max stress plateau (which is not reached in practise)
11. Challenges:
 

* CCR + Stretch	* CCR in LCB polymers	* snipping' for fast flows?
* Getting reversing flow predictions right (c.f. die swell)		* Coupling in complex LCB structures
* Computable versions of molecular CE's		

#### *Around Olley presentation*

1. Best separable KBKZ fits, where planar vortex growth is properly predicted, tend to have N1 wrong or stress rise wrong
2. A question was asked if the Pom-pom approach might lead to multiple solutions.
3. Weissenberg no (We, Wi, Ws..) are not easily defined for multimode?

4. Engineering aim to predict melt flows is being met; Physicists aim to predict rheology – not met yet
5. Modellers are looking at:
  - time-wise stress filtering
  - true time stepping
  - treat as a solids problem?

*Around Mitsoulis presentation*

1. Joseph generic model (1993) provided a route to categorising various CE's
2. Integral approach followed because of (a) FE method; (b) Galerkin discretisation of conservation equations (c) particle tracking for extra stress tensor; (d) streamline integration
3. Pressure calculation most error prone (cf CE !)
4. For the same problem the number of degrees of freedom is for integral equation modified KBKZ similar to or lower than for multimode pom-pom
5. KBKZ equation is limited – needs evolution equation too.

*Around Harlen presentation*

1. Stress is dependent on local strain rate – carries information with it = Lagrangian
2. Velocity and pressure calculated using standard FE techniques; stress calculated in a Lagrangian frame
3. Problems are very large deformations (leading to mesh distortion) and fluid advection (leading to loss of resolution in areas of interest)
4. Rasmussen & Hassager (1993; Hassager from 83 on) have integral models, with strains interpolated onto a new grid once elements become too distorted – fully 3-d model now working well;
5. Cons of current Lagrangian approach:
6. Low order elements used (lower accuracy)
7. Grid is not fixed wrt boundaries
8. Require new elements at inlets, remove elements at outlets
9. Pros of current Lagrangian approach:
10. Solve CE in natural Lagrangian frame
11. CE's can be translated into Ordinary Differential Equations (ODEs) – quick to solve
12. Therefore can use complex multimode CE at almost no extra cost (most of computational time is spent on the Stokes solver – cpu time  $\sim N^{1.5}$ , memory required  $\sim N$ )
13. New or modified CE's are easy to add
14. Ideally suited to free surfaces
15. Curved elements desirable at boundaries?
16. Benchmark flow required for different approaches
17. Current pom-pom differential approach leads to 'coarser' results (approximations from converting from integral to differential form of CE)

*Around Laun presentation*

1. CE for what? - Main need for industry is to provide accurate simulation.
2. BASF using original Wagner approach + Polyflow
3. Obtaining reliable data for CE's is an underestimated task – takes  $\sim 1$  year to get a reliable data set.
4. Problem of matching data with predictions (e.g. commercial solver results were not possible at higher flow rates; so used time-temperature superposition)
5. Example of quality of rheological data required – two data sets provided fits, but with very different parameters!
6. Painstaking oil-bath extensional rheometry and RME data now agree – RME must have true deformation of samples measured by imaging (not inferred from set points; typically strain rates in RME are less than set strain rates) – RME optical 'control' vital.
7. Example of PA6 spinning - can't get off line rheometry ( $G'$ ,  $G''$ ) at desired rates; one approach is to derive moduli from viscosity function.
8. Matches between off line rheometry and process conditions? – shear may go to very high strains; extensions are lower strain but often at much higher strain rates than in off line tests
9. If rheology data is obtained at a low T (e.g. for RME force measurement reasons) there is the potential problem of memory effects.

*Around Debbaut presentation [A bridge – “we don't make polymer and we don't produce CE's”!]*

1. 'Solver' should be separated from FE algorithm

2. CE could be viewed to be of a fluid (of interest to fundamental understanding) – or of a flow (of interest to a processor) - e.g. don't need extensional viscosity for die swell predictions?
3. Latest modifications (e.g. Eindhoven) of multimode pom-pom have some attractions, but molecular feature detail is being lost (as  $I_A = \lambda^2$  is assumed – this re-connects stretch and orientation, reduces to a Maxwell equation), also  $N_2$  not zero; however, lots of degrees of freedom, useful in polynomial form
4. Consider other possible CE's – e.g. Leonov model?
5. What is the relevance of simplified CE's (c.f. scalar approach – allows very fast solving) – noting that generalised Newtonian models are used to calculate die flows (but can't do more sophisticated things, e.g. normal stresses) – see comments on Injection Moulding above!
6. It would be useful to have a benchmark flow other than the 4:1 contraction – preferably with industrial relevance. But problems of complexity if extrudate is included, c.f. phase changes.
7. [Debbaut: The question of the well-posedness of the steady state flow calculation with the pom-pom equation were raised, where the orientation tensor  $S$  is evaluated as  $A/\text{tr}(A)$ . This is not to imply that there is a problem, but the question needs to be raised]

[In addition, *Dr Ashish Lele, Cambridge University*, wrote: “One point about the CEs which we actually never got to discuss in the workshop is about the incorporation of MWD in molecular CEs in a self-consistent manner. The Pom-Pom and the MSF CEs take into consideration the MWD through a spectrum of relaxation times. However, there are certain issues in using this approach on which some comments from the experts would be greatly appreciated:

- a) While the relaxation times calculated from LVE data could be assumed to represent an orientation time for each of the molecular weight fraction, this approach does bring in some phenomenology into the "molecular" CE. I am also not sure whether the smallest relaxation times (such as say, of the order of 0.01 s) would really represent a 'reptation' time since the corresponding chain lengths might be too small to really have even 10 entanglements.
- b) The memory function can reduce to the simpler  $\exp(-t')$  form for the simpler DE model. However, once the other relaxation mechanisms such as CCR or retraction are incorporated in the segment renewal probability equation then I don't think one can represent the memory function by the simple exponential form anymore. So for molecular CEs that try to incorporate CCR, how can one account for MWD effects?
- c) It would be nice to know what is the status of the "molecular" approach for incorporation of MWD effects, such as the double reptation concept that is being considerably discussed in several papers these days.

Could you kindly circulate this question among the COMPRO participants. I would like to hear some comments on them. “]

[*Benoit Debbaut, Polyflow* also noted “ I believe that this kind of workshop is extremely important, and should perhaps attract more people from the industry. I believe indeed that significant achievements can be made through a well managed communication between academia and industry, and that exchange of questions, answers and knowledge between both parties should be pursued.”]

Many thanks to all who provided corrections and further comments, or encouragement!

I have not received slides from all speakers, and decided that this would in any case not be a very efficient way to share information; perhaps we could use the COMPRO web site, with a private area, to share such information.

I hope that this meeting provides a stepping stone to a further gathering, to develop the spirit of our discussions. Again, I much appreciated the contributions from speakers and attendees, which made the event so worthwhile.

Phil Coates, 21 February, 2001