

Basic Polymer Rheology, as related to Extrusion Coating Machinery

David R Constant

Battenfeld Gloucester Engineering Co. Inc.

Gloucester, Massachusetts, USA

Abstract

LDPE remains the classic material of choice for many Extrusion Coating Applications, due to excellent processing and end-use performance reasons. High shear extrusion screws are desirable, actually promoting oxidation of the melt for improved adhesion to substrates. T-shaped flat die technology, with internal deckling, has emerged as the premium technology to handle monolayer and multilayer extrusion coating applications with LDPE and other polymers. But as with all technologies, remaining competitive means meeting demands for improved products, at higher rates and at lower cost. In this case this also means machinery suppliers need to understand machine “innovation’s” effects on the polymers.

Higher rates cause higher “extension” of the melt from the die, which will affect melt orientation, neck-in, melt resonance and overall quality and productivity. Traditional measurements of Melt Index do not quantify effects on the polymer and the process. Measurements of melt strength, or melt elasticity are therefore necessary as a Q.C. tool for existing operations and for design reasons for new equipment.

Introduction

Extrusion coating and extrusion lamination are important conversion processes for the production of many packaged food or industrial products. Extrusion coating involves application of a molten layer of polymer, usually low density polyethylene (LDPE), acid copolymers like ethylene acrylic acid (EAA) or ethylene methyl acrylate (EMA), and “newer, modified” LLDPEs to a substrate such as paper, paperboard, aluminum foils and various other polymers such as oriented polypropylene (OPP) or oriented polyethylene terephthalate (OPET). [1, 2] Related applications include milk cartons, single serve milk and juice boxes, snack bags, tarps, and tapes. The total world consumption of extrusion coating grade polyethylenes has been reported as being ~ 1.8 million metric tons in 2004 [3] and continues to grow at ~ 3% annually. [4]

In the extrusion coating process, the molten polymer is extruded through a slot die with a die gap of typically 1mm (1000 microns), while the width typically ranges from 1 – 3 m, sometimes wider. To obtain a typical coating weight ranging between 10 – 50 g/m² (~ 10 – 50 microns, for LDPE), coating rolls velocity needs to be in the range of 400 – 600 m/min, drawing the melt through an air gap of ~ 250 mm from the die opening to the coating roll. This means the melt “curtain” must be drawn ~ 100 x, i.e. very high “extension” of the melt condition. Actual extrusion coating operations also involve cooling of the melt before it contacts the substrate and solidities, i.e. non-isothermal effects.

Unfortunately, such extension, or elongation of the melt, tends to promote “neck-in” and edge beading (thick-thin sinusoidal events sometimes referred to as dog-bone effects. [5, 6] This phenomenon has been studied significantly and the words extension and elongation are used interchangeably.

This paper is intended first to provide an overview of rheology measurements typically used for extrusion coating resins, primarily including Melt Index (MI) and capillary rheology data, which are generally satisfactory for most extrusion coating operations. Capillary data can, for example, be used to calculate elongational data, useful for comparing relative performance of various polymers. Another quantitative tool presented is melt tension, where data are generated from a molten strand pulled through air and wound at increasing acceleration until failure. [7, 8] Lastly, a novel approach using dynamic plate-plate rheology data is also introduced, where melt strength (or melt elasticity) is reported vs. melt viscosity, to provide relative comparisons of polymers.

Classic capillary data tends to be most used for flat die design, providing the critical inputs for commercial, computational fluid dynamics software programs. Elongational data is less used commercially today, although available, because of “difficulties” to generate reliable data that are “universally accepted”. Elongational rheology data clearly has implications regarding performance in high speed extrusion coating, however, as has led to dies now available for edge bead minimization, edge encapsulation and dies for minimizing multi-layer instabilities. [9] “Higher” pressure drops are calculated in dies when elongational data are included, telling designers the need to consider ways to provide significant die exit pressures for consistent operations. [10]

Rheological Methods available, by definition

Melt Index, (ASTM D 1238): provides one point data, at a pre-determined imposed melt temperature, using a pre-determined mass to convey melted polymer through a cylinder. (Fig. 10) For polyethylene, those conditions include 190C, 2.16 kg and a heated 8 mm cylinder of 2.1 mm diameter.

Capillary Rheology, (ASTM D 3835 and D 5422): provides melt viscosity, sensitivity (stability) of melt viscosity with respect to temperature and polymer dwell time, die swell ratio, melt density and shear sensitivity measurements when extruding under a constant rate or stress. [11] Basically, the use of entrance and exit pressure transducers in a heated cylinder equipped with applied force technology (i.e. gear driven motor, or an extruder) provides for more complete data generation. (Fig.11 & 13) Viscosity vs. shear rate data up to 1000 s^{-1} is commonly measured. Elongational data can be calculated as well, using empirical relationships like developed by Cogswell. [12]

Melt Tension: was originally developed by Meissner [13], published in 1971. The test essentially pulls molten polymer extrudate from a capillary rheometer through two rotating wheels, drawing down the polymer with a defined velocity, producing elongational deformation. A force is recorded which allows for relative comparison of polymers. (Fig. 23 & 24)

Dynamic Rheology, (ASTM D4065 and D4440), provides very low shear data collection with several physical variations of the apparatus commercially available for measuring polymer melts. Complex viscosity, elastic and viscous moduli data are generated using frequency sweeps, fixed temperature or temperature sweeps, fixed frequency. Tan Delta, the tangent of the phase angle, is the ratio of viscous modulus to elastic modulus, and is a useful quantifier of the presence and extent of elasticity in a polymer melt. Parallel plate geometry (25 mm) was selected for this particular work, specifically using the Rheometrics Scientific ARES apparatus, at 5% strain. (Fig. 25)

Rheology as a Q.C. Tool

Although MI is the traditional test method employed by extrusion coating manufacturers, its one point shear rate limitations are clear. For a 10 MI LDPE tested at “standard conditions”, shear rate calculates to 24 s^{-1} ; for a 1 MI the calculated shear rate is 2.4 s^{-1} . Since most extrusion processes operate at shear rates often range up to several hundred s^{-1} or higher, this single point measurement is clearly limited in predicting the process.

A better measurement methodology is capillary rheology, which can differentiate between different polymer’s viscosities vs. shear rates quite well, but it has limitations at very low shear rates ($< 10 \text{ s}^{-1}$). In the case of LDPE, it might possibly differentiate between certain supplier’s LDPEs, i.e. between broader or narrower molecular weight distributions (MWD). See Fig. 17 for related equations.

Both of the above methods, though, do not directly account for the case where the melt is extended from the die, i.e. extrusion coating. In addition, both methods do not quantify the effects of drawing the melt in non-isothermal conditions.

Data generated using capillary rheometry, however, can also be used to calculate elongational viscosity, elongational stress, recoverable elongational strain, elongational modulus and even die swell. See Fig. 22 for

calculations. And a melt tension apparatus can be connected in-line to the capillary rheometer to provide melt tension data if desired. These types of data can be practical to generate in a production laboratory.

Dynamic rheology has emerged as the most elegant of techniques, but it is more demanding for technical resources for interpretation and reporting of the data. It truly measures the elastic modulus component G' and viscous modulus component G'' , plotting the data along with complex viscosity of the melt, vs. frequency (shear rate). [14] The data can then be used to quantify elastic and viscous relationships at selected temperatures to essentially “rank” polymers for extrusion coating processing performance. (Fig. 26-29) Please note that a 2 MI LDPE was selected as a “reference” material, known to have excellent melt strength due to branching., and all other polymers have been compared to this one.

Computational Models “Overview” and Die Manufacturer’s Inputs

Information was gathered from two major extrusion coating die manufacturers,, both from the USA, to learn specifically about the use of commercially available software, or of their own techniques for die design. Both companies are well aware of two prominent software packages for die design, specifically Compuplast Canada [15] and Fluent’s Polyflow. [16, 17, 18] And both softwares reportedly have 2-D Finite Element Analyses (FEM) mesh capabilities for die design. Although the die manufacturers do see the value in the commercially available softwares in analyzing their own designs, both prefer their own internal programs for die specification and production.

Classic capillary rheometry values of viscosity and shear rate at given temperatures are primarily used for design inputs, but elongational data are for the most part ignored or not fully developed. Today’s designs have essentially “evolved” through decades of experience and performance is again reportedly sufficient. There is an awareness of the value of elongational data, where elasticity of the polymers can and do influence flow. Intuitively, leading die designers therefore always strive to eliminate sharp corners and rapid transitions in their designs, to allow them to “minimize” extensional deformation within the die. As such, they feel they do not need to worry about elongational effects.

Continuous improvement on die design, however, remains an objective of world class die manufacturers. Performance is always the ultimate answer, but linking polymer observed elongational attributes to that performance promotes further improvement opportunities to the design. Three such commercial examples include the following:

- End encapsulation, where branched polymer (LDPE) with high elongational modulus (high melt strength) significantly reduces neck-in in multi-layer cast film applications, which could include multi-layer extrusion coating applications (Fig. 32)
- Internal Deckles design development to minimize edge bead on cast film and extrusion coating dies (Fig 33)
- Allowing for increased pressure drops within the die to make sure adequate die pressure is available at the die exit to produce a uniform melt curtain from T-dies (Fig. 7)

From a new product (die design) development perspective, since extension of the melt is inherently part of the processes of cast film and extrusion coating, the question of what die design parameter(s) could improve output and maintain quality of the extrudate still lurks within the R&D sector.

Potential considerations:

- die gap (already adjustable, no design work needed)
- die width (pressure drop calculations depend on the application need)
- further enhancements to end capsulation, wider, narrower, depending on the intended polymer
- die land length(s), within limits

Since the first two points are not really options, some die manufacturers have focused recently on the latter two considerations, End encapsulation is now quite well known and implemented, although there is always room for improvements.

Die land lengths are less studied and understood. Arguments have been made for “shorter” land lengths and “longer” land lengths, but few reported experiments are conclusive. The relationship of die swell to MWD and/or branching is clear and well known, but relating die swell to elongational data and then to Neck-In requires interpretation and further study, and remains open to debate. Many factors can distort data generated.

In theory, though, through the interpretations of data as presented in this paper:

- Decreased land lengths generally contribute to increased die swell, which can be associated with increased Elongational modulus. This should translate to decreased Neck-In.
- Unfortunately, even if proven so, a secondary problem could develop with very short land dies, assuming pressure gradients are acceptable. That secondary problem could be die lip build-up, caused by high die swell, especially at today’s ever increasing outputs, where the polymer actually swells over the outside of the die lips to the point of sticking to the hot metal on the outside of the die.
- Balancing Neck-in with die swell therefore remains a compromise in die design.

Summary and Conclusions

Extrusion Coating represents one of many extrusion processes where molten polymer is “drawn” from a die. High extensional rates are encountered, at non-isothermal conditions, especially at today’s production output speeds. Understanding the polymers used for the process, as well as the process itself, including relevance to proper design, is critical to success in commercial operations.

Characterization tools beyond melt index are useful for best distinguishing incoming lots of specific polymers used. Capillary rheology techniques are most easily implemented in a production environment, and could be sufficient to measure viscosity vs. shear rate and shear stress vs. shear rate at selected temperatures, as well as die swell and melt density. Calculations for elongational properties can also be made. And addition of a melt tension device can be easily accomplished if this technique is preferred to calculation of elongational properties. A direct measurement of melt strength can be measured by melt tension testing. Such properties can be useful in a Q.C. department for qualifying incoming polymers.

Dynamic rheology is a more elegant tool, offering ways to rank elastic properties concurrently with viscous properties of the melt. Techniques are shown.

Relating the rheology to design is more complicated, however, as might be expected. For screw design, the issue is not as apparent, because designing high shear screws by decreasing clearance between screw flights is relatively straightforward. For die design, although significant effort has already been spent towards understanding the elastic component of visco-elastic polymer melts, capillary rheology for the more “known” viscous measurements is the standard. Complexity in measurement and non-standardized procedures limit use of elongational data and empirical studies are often incomplete due to numerous variables available to investigate.

Nonetheless, research continues in this field, as both understanding of polymer rheology, polymer processing and computational models further develop, driven by the need for continuous improvement in productivity.

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Figures

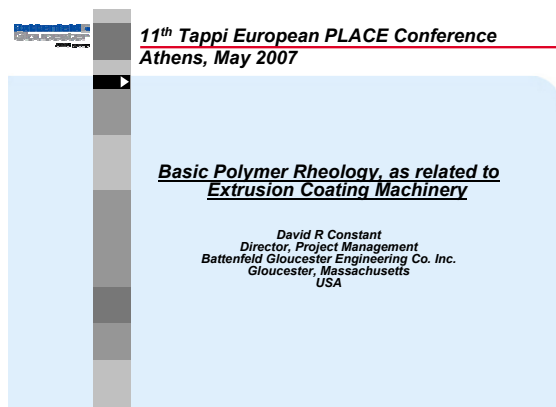


Fig.1

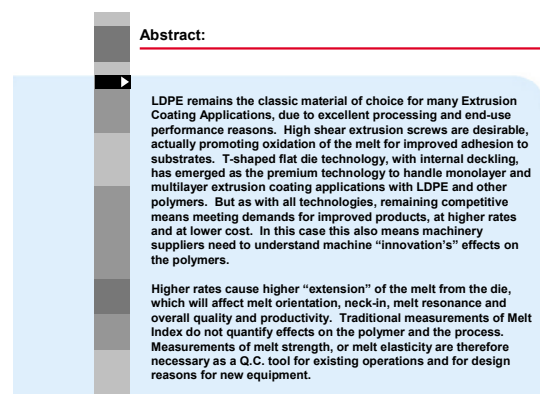


Fig. 2

Extrusion Coating Carriage (EU Installation)
Front & Back views

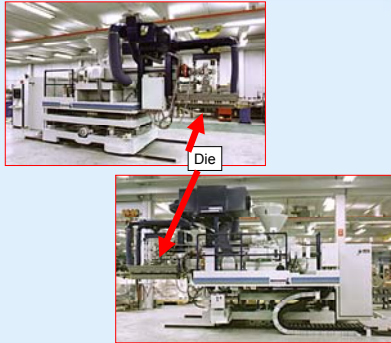


Fig. 3

Extrusion Coating Carriage and Die (USA Installation)



Fig. 4

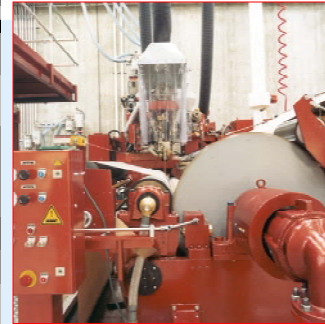
Die and coating station...



Coating station Ref.: Polytype, Switzerland

Fig. 5

Coating station...



Coating station Ref.: Polytype, Switzerland

Fig. 6

Die Designs will affect flow...at least until the die exit...

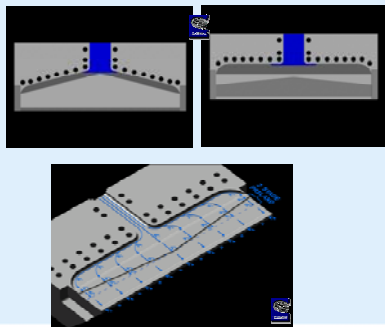


Fig. 7

Neck-In and edge weave are typical issues to deal with in Cast Film and in Extrusion Coating applications.

$$NI = \frac{\omega_{die}}{\omega_{film}}$$

Where: ω = width



Neck in (NI), cast film line

Draw Resonance / "edge weave" can occur when reaching a critical shear stress

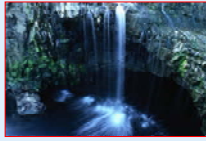
Fig. 8

Basic Polymer Rheology

The word **Rheology...**

is of Greek origin "Rheos",

the study of flow

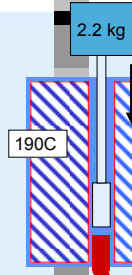


Measurements:
 capillary, including Melt Index, and die swell
 capillary + melt tension, including extensional measurements
 dynamic rheometry, including extensional measurements

Basis:
 Viscosity (η) = shear stress (σ) / shear rate ($\dot{\gamma}$)
 where: (shear stress = force/area, shear rate = displacement / original length)

Fig. 9

Melt Index, the standard Measurement

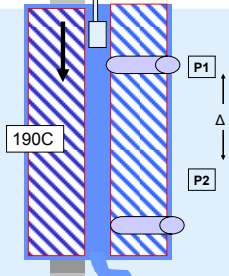


- Is an indirect measurement of MW
- Is expressed as g/10 min (or dg/min)
- Is limited in info provided, i.e. is at low shear ($\ll 10 \text{ sec}^{-1}$)
- Is a one point only measurement
- For Polyethylenes, is measured at 190C, 2.16 kg
- Is not representative of extrusion, where shear rate is more typically 10 to 100 or even up to 1000 sec^{-1}
- Can be deceiving where MWD for a given MI is "different"
- LDPE from autoclave reactor is "broader" MWD than LDPE from tubular reactor (different catalyst systems, process manufacturing conditions)

Polymer extrudate: g / 10 min.

Fig. 10

Classic Capillary rheometer

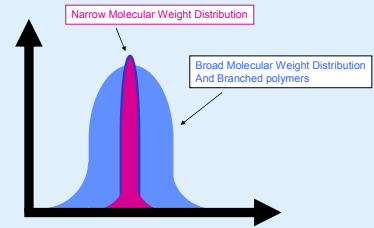


- Measures pressure drops (ΔP) in the cylinder to calculate viscosity vs shear rate
- Data also used for elongational calculations

Polymer extrudate

Fig. 11

Molecular Weight Distribution: one of many polymer factors affecting polymer swell and polymer melt strength...



As an example, although Melt Index (indirect measure of Molecular Weight) may be the same for two different LDPEs ..., MWD may be very different

Fig. 12

Viscosity vs Shear Rate of Common Packaging Resins

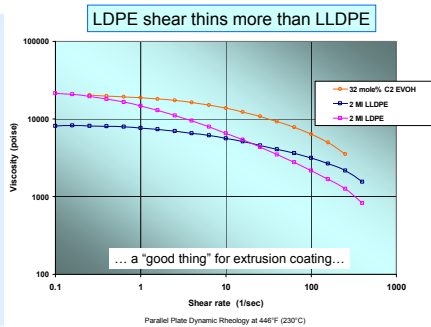
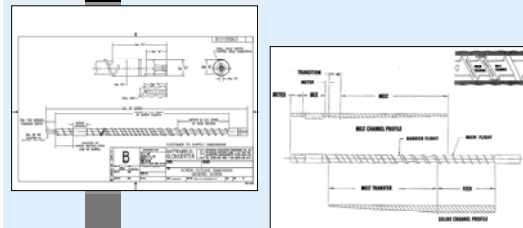


Fig. 13

Variable Lead Barrier Screw High Shear specified for Extrusion coating



Low flight clearance, promoting shear thinning and oxidative degradation, is desired for extrusion coating screws

Fig. 14

Melt Strength: Critical for most extrusion processes

where molten polymer is "drawn" from a die

Correlates with:

- Bubble stability in blown film
- Neck-in seen in cast film and extrusion coating
- Draw resonance / Edge-weave in cast film and extrusion coating
- Overall extrudate melt quality

Is affected by the polymer:

- Molecular weight (MI)
- Molecular weight distribution (MWD or Polydispersity Index)
- Branching (vs. linear) molecular structure

Fig. 15

Extensional Flows consider the elastic element...

Applied Stress

NECKING

- Tension thinning
- point stretching, weakens
- low melt strength

Uniform draw

- Tension stiffening
- constant thickness change
- toughens until elastic failure
- high melt strength

Ref: Polymer Melt Rheology, Cogswell 1994

Fig. 16

Common used fixed geometry equations (for a slot die)

Flow in a die is affected by:

- The polymer itself
- The melt process temperature
- The shear stress and shear rate of the process, "within the die", as set by the output of the system

Die shear stress = $\frac{t_1 P_1}{2 L_1}$

Die shear rate (s⁻¹) = $\frac{6 Q}{t_1^2 (W + t_1)}$

Where:

- Q = volume flow rate through the die (cm³ / sec)
- L₁ = die land length (cm)
- W = width of slit die (cm)
- t₁ = die gap (cm)
- P₁ = pressure drop over land length L₁ (kg / cm²)

Source: Plastics Engineer's Data Book, Glanville, 1971

Fig. 17

Inferring Elastic Modulus from post extrusion swelling...

- If increased die land length should decrease die shear stress...

land length = shear stress = die swell

- And conversely, increased shear stress through the die should mean increased die swell at the die exit...

land length = shear stress = die swell

Fig. 18

Die Swell & Elastic Response relate to Extensional Flow

IF... Increased die swell ~ Increased Elongational Stress (σ_E)

and..... Increased (σ_E) = Increased Elongational Modulus (E)

as deduced from: $E = \sigma_E / \epsilon_R$

(where ε_R is elongational strain)

Polymer Flow

Less "elastic" polymer...

More "elastic"... die swell

Which follows the empirical observations...

(E) = Melt Strength (M.Str)

and

(M.Str) = Neck-In (NI)

Fig. 19

Inferring Elastic response from die swell data...

Effect of die length-to-radius ratio on post-extrusion swelling: polypropylene at 210C

Which follows with:

Decreased land length = higher die swell = lower neck-in

Reference: Polymer Melt Rheology, Cogswell, 1994

Fig. 20

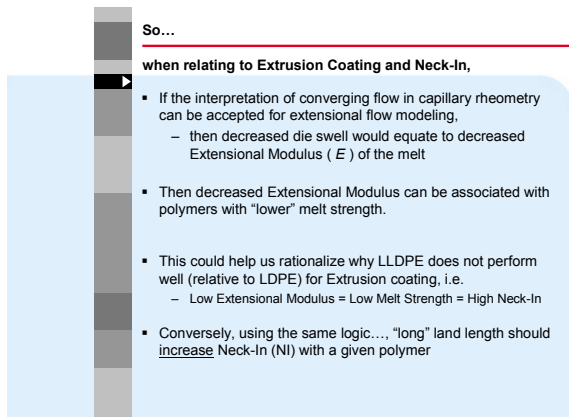


Fig. 21

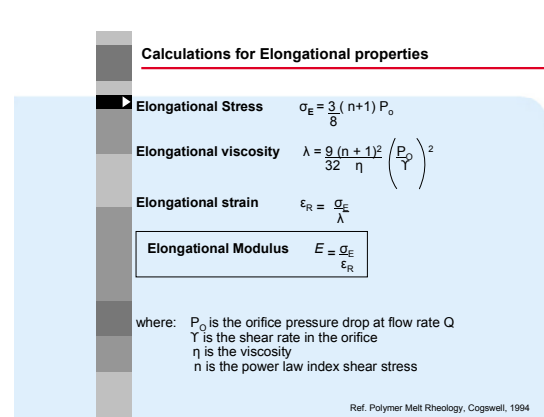


Fig. 22

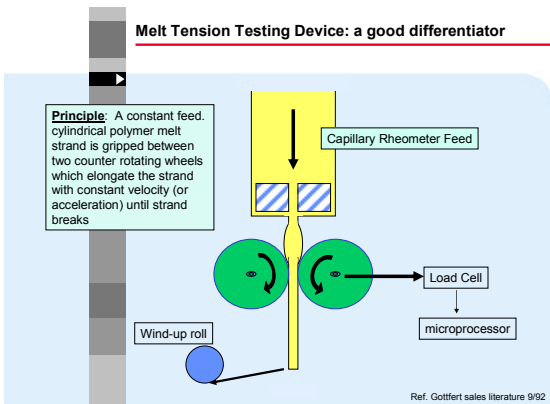


Fig. 23

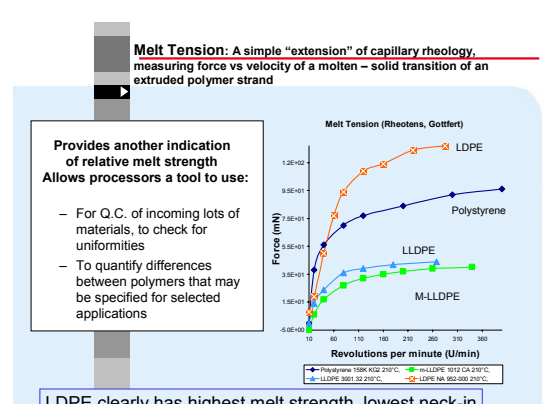


Fig. 24

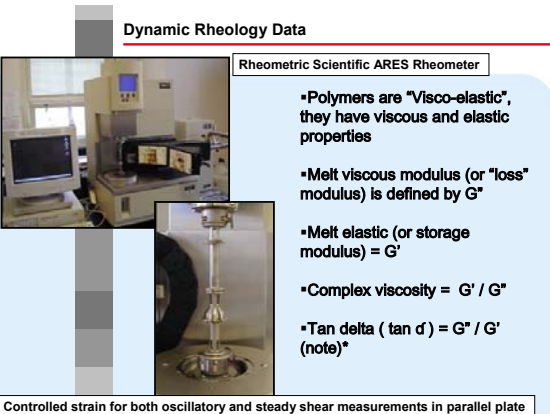


Fig. 25

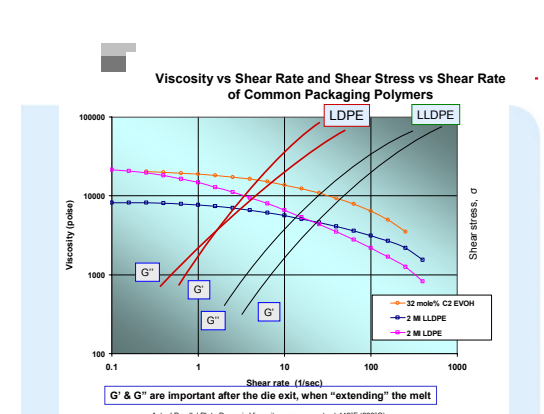


Fig. 26

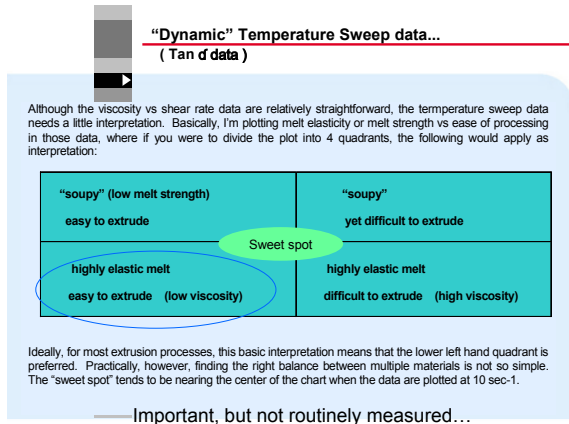


Fig. 27

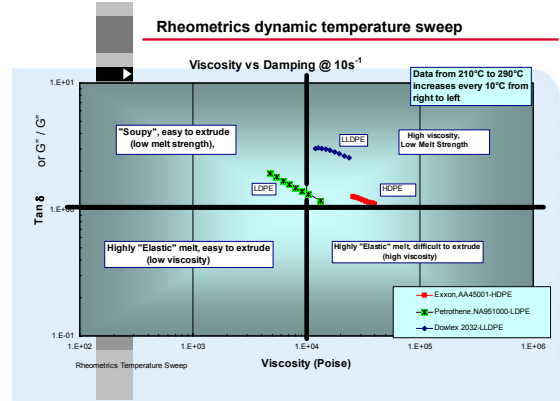


Fig. 28

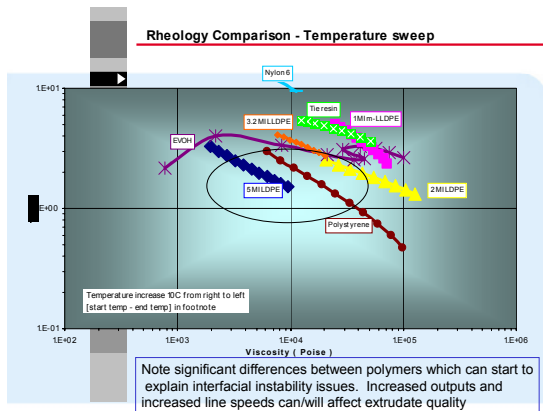


Fig. 29

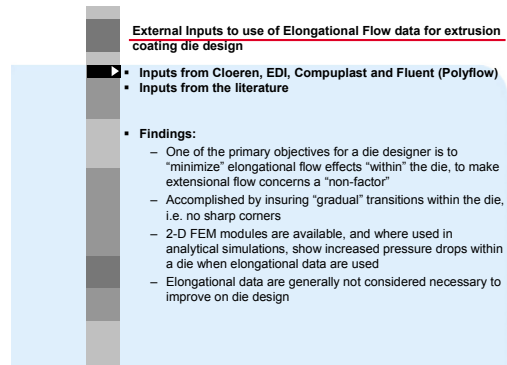


Fig. 30

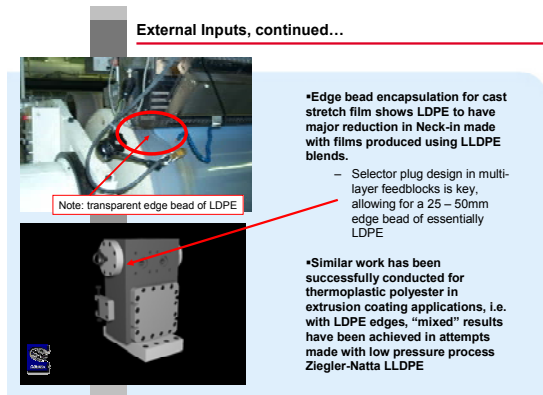


Fig. 31

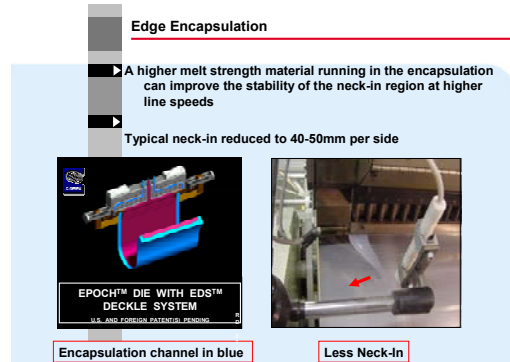


Fig. 32

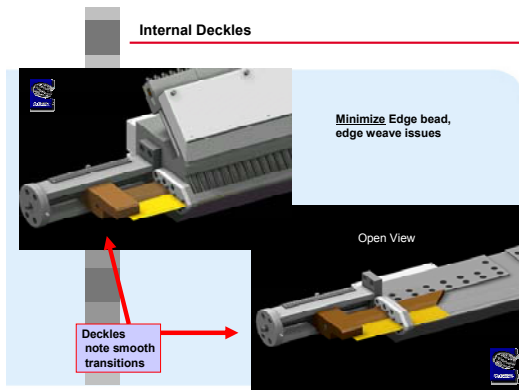


Fig. 33

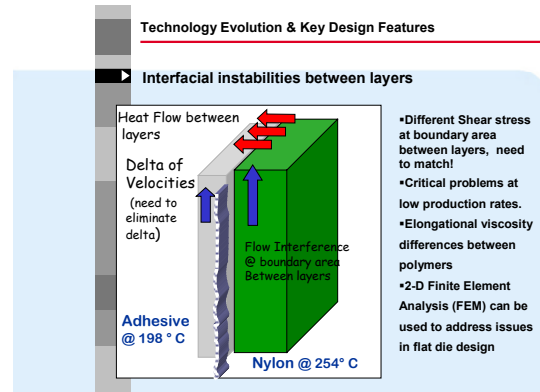


Fig. 34

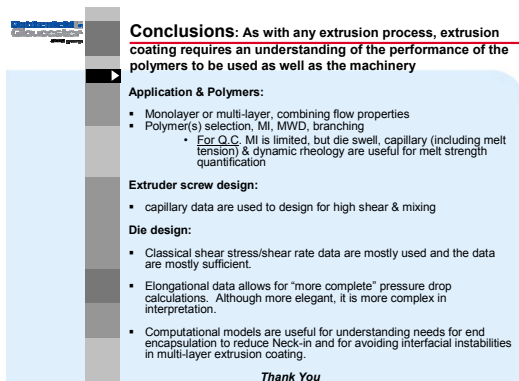


Fig. 35