MODIFICATION OF THE PTT MODEL FOR THE PREDICTION OF ELONGATIONAL VISCOSITY AND ITS APPLICATION TO THE FILM BLOWING PROCESS

A Dissertation
by
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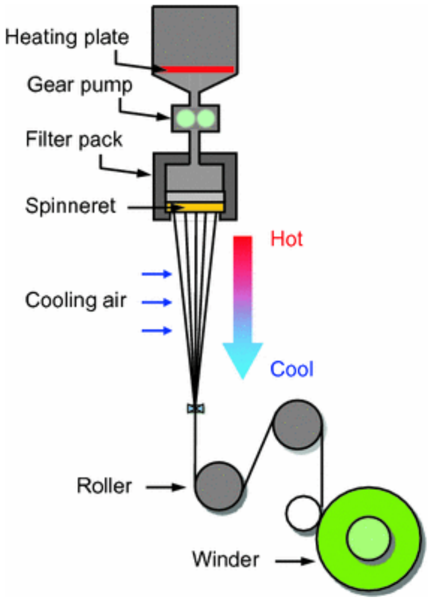
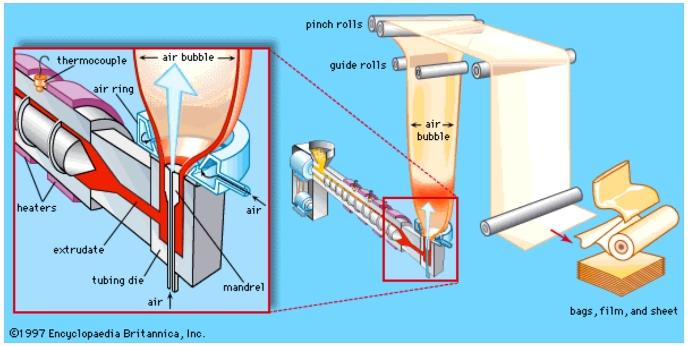
Importance

Whenever molten polymers are stretched, the elongational viscosity plays a very important role*1 for controlling the process, designing of equipment, evaluating resins´s behavior and, why not, tailoring them.





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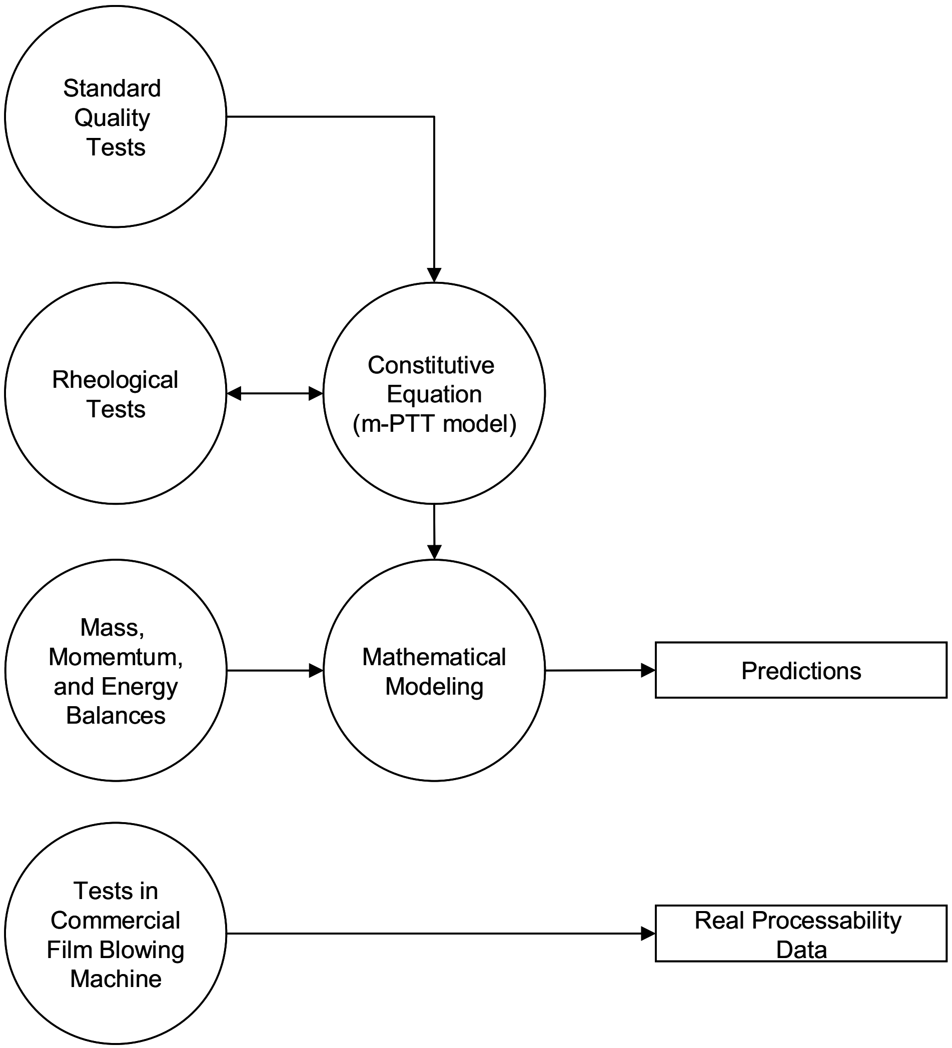
Objectives

- To obtain a general model, based on material properties, able to predict elongational viscosity for polyolefins.
- To use this model to predict processability, specifically for the film blowing process.
- To tailor materials with specific properties

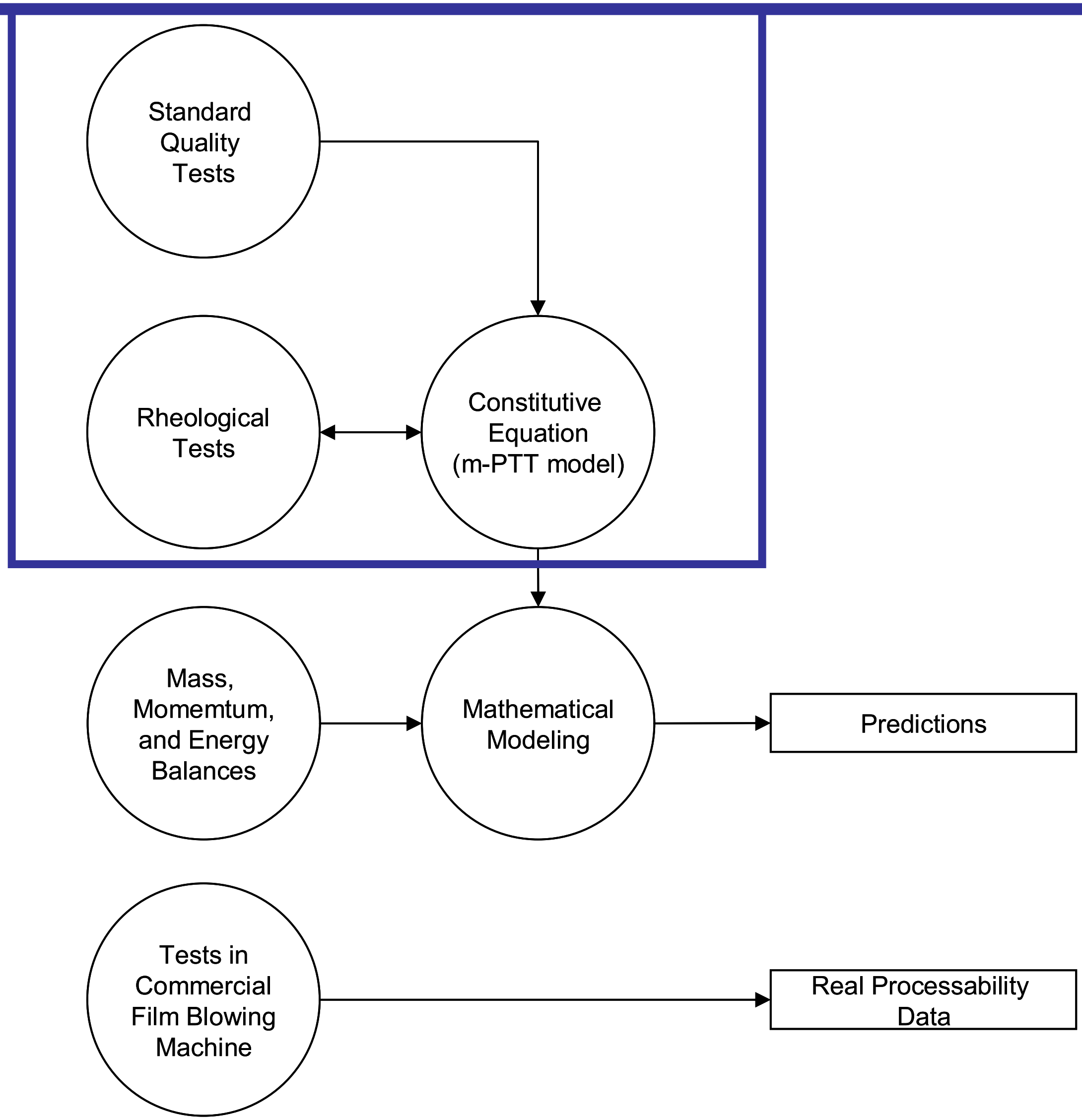
Overview


Standard Quality Tests
Rheological Tests
Constitutive Equation (m-PTT model)
Mass, Momemtum, and Energy Balances
Mathematical Modeling
Predictions
Tests in Commercial Film Blowing Machine
Real Processability Data

Outline

- Modification to PTT model
  - Background
  - Hypotheses
  - Experimental
  - Model Conceptualization
  - Predictions
- Film Blowing Modeling
  - Background
  - Model
  - Materials and Methods
  - Predictions
- Conclusions and Recommendations

Focus on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Tests in Commercial Film Blowing Machine
Real Processability Data

Background

Researchers	Year	Comments
Phan Thien and Tanner	1977	A new constitutive equation based on network theory was presented.
Phan Thien *	1978	The PTT model is used to simulate the fiber spinning process.
Larson	1984	In spite of presenting limitations, the PTT model was identified as one of the best constitutive equations for the prediction of elongational properties.
Stephenson	1986	Model predicts overshoots that are not observed in reality.
Cortes and Bonilla	2004	Even though the PTT model worked fine for i-PP, it failed to predict accurately the elongational viscosity of s-PP. Then, using MWD averages, a modification to the model parameters was proposed.

* Several researchers, such as Devereux *et. al.* (1994), Ching *et. al.* (1996), and Mier *et. al.* (2000), have used the PTT model in the modeling of the fiber spinning process with satisfactory results.

Background

$$Z(tr\tau_i)\tau_i + \lambda_i\tau_{i(1)} + \frac{\xi}{2}\lambda_i\left(\dot{\gamma}\cdot\tau_i + \tau_i\cdot\dot{\gamma}\right) = -\eta_i\dot{\gamma}$$

$$Z(tr\tau_i) = \exp\left(\frac{\alpha\lambda_i}{\eta_i}tr\tau_i\right)$$

$$\tau = \sum_{i=1}^{N}\tau_i$$

$$Z(tr\tau_i) = \exp\left(-\frac{\alpha}{G_i}tr\tau_i\right)$$

	parameters	comments
original	$\xi = constant$ $\alpha = constant$	• Shear parameter causes violation of Lodge-Meissner relationship. • The model fails to predict η_e of s-PP resins. • Larson (1988) and Stephenson (1987) proved that it presents significant limitations.
version 1	$\xi = 0$ $\alpha = f(\dot{\varepsilon}, M_z, M_e)$	• According to Larson (1988, 1998) the shear parameter was set to zero. • Using i-PP and s-PP, it was found that α is a function of the extension rate and MWD
version 2		• The same study was extended to HDPE and PS. • The modified model failed, but it was found that each type of polymer presents ad specific function. • An empirical relationship between α and Mw was found. • The model allows the prediction of η_e (+/- 10%) from just Mw and the discrete relaxation spectrum

Background

$$\tau = \sum_{i=1}^{N} \tau_i \qquad Z(tr\,\tau_i)\tau_i + \lambda_i \tau_{i(1)} + \frac{\xi}{2}\lambda_i\left(\dot{\gamma}\cdot\tau_i + \tau_i\cdot\dot{\gamma}\right) = -\eta_i \dot{\gamma} \qquad Z\left(tr\,\tau_i\right) = \exp\left(-\frac{\alpha\lambda_i}{\eta_i} tr\,\tau_i\right)$$

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version 2	$\xi = 0$ $\alpha = f(\dot{\varepsilon}, M_W)$	• The same study was extended to HDPE and PS. • The modified model failed, but it was found that each type of polymer presents ad specific function. • An empirical relationship between α and Mw was found. • The model allows the prediction of η_e (+/- 10%) from just Mw and the discrete relaxation spectrum

Background

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version 1	$\xi = 0$ $\alpha = f(\dot{\varepsilon}, M_z, M_e)$	• According to Larson (1988, 1998) the shear parameter was set to zero. • Using i-PP and s-PP, it was found that α is a function of the extension rate and MWD

$$\alpha = -0.0504\ln(M_W)\ln(\dot{\varepsilon}) + 0.6279\ln(\dot{\varepsilon}) + 0.1142\ln(M_W) - 1.3155$$

Hypotheses

- There is a function describing the interactions of a set of self-avoiding walks “chains” and the change of such interactions after an imposed deformation, that is directly related to the rate of creation and destruction of junctions in the Z function of the PTT model.
- The parameters of such function are related to MWD features and/or material functions.
- The elongational viscosity can be estimated with a modified PTT model obtained from the previous hypotheses.
- By coupling the m-PTT model with process dynamic equations, it is possible to predict film blowing processability.

Experimental

- Capillary Rheometer
- Oscillatory Rheometer
- Constant Stress Rheometer
- Standard Quality Properties

- Materials:

UNIMODAL
- 12 i-PP
- 4 s-PP
- 6 PS
- 9 HDPE

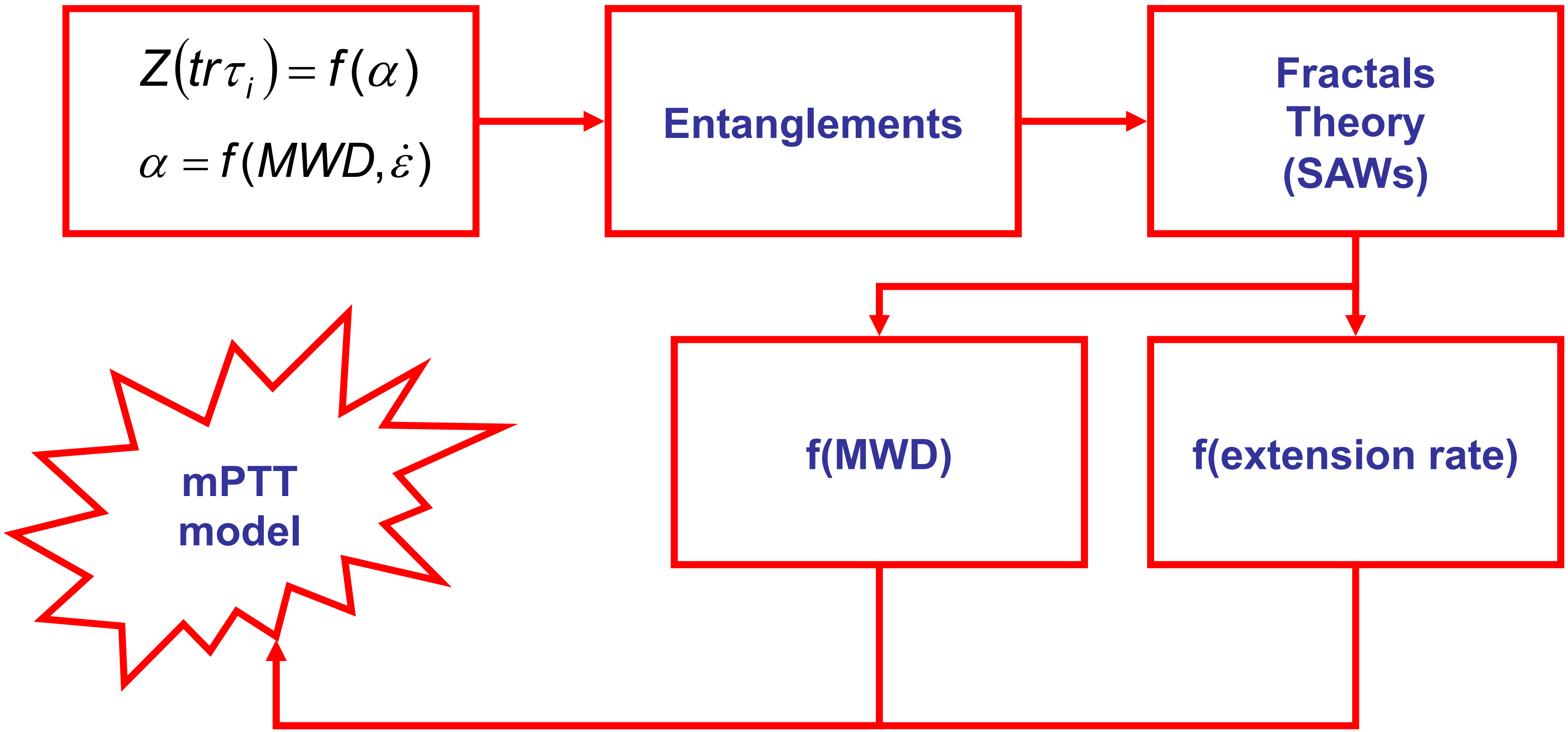
Model Conceptualization

- α in the PTT model is a fundamental part in the rate of creation and destruction of junctions.

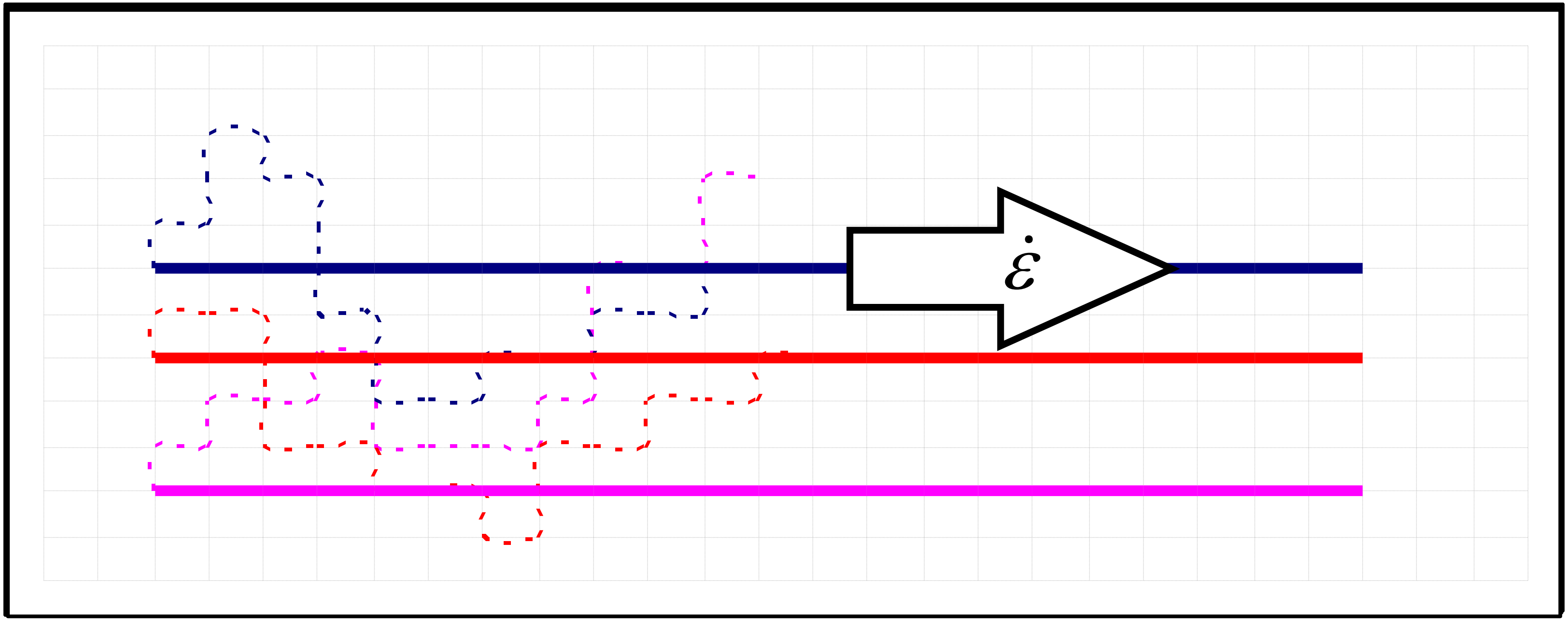
$$Z(tr\tau_i) = \exp\left(-\frac{\alpha}{G_i} tr\tau_i\right) \qquad \alpha = -\ln\left(Z\left(tr\tau_i\right)\right)\frac{G_i}{tr\tau_i}$$

- Phan Thien and Tanner (1978) defined α just as an “elongational parameter”.
- Need to understand the general functionality of entanglements.

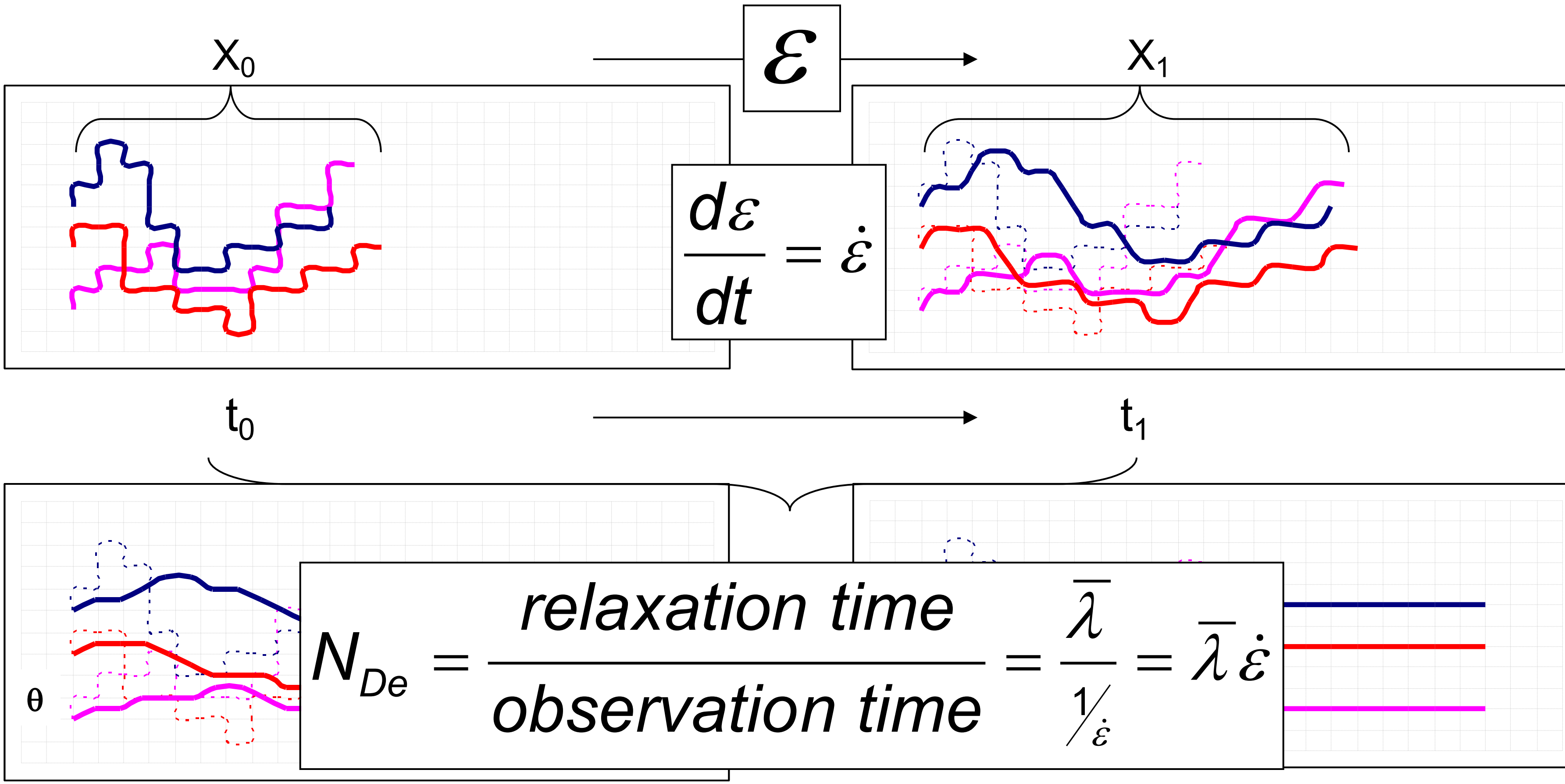
Model Conceptualization



Model Conceptualization



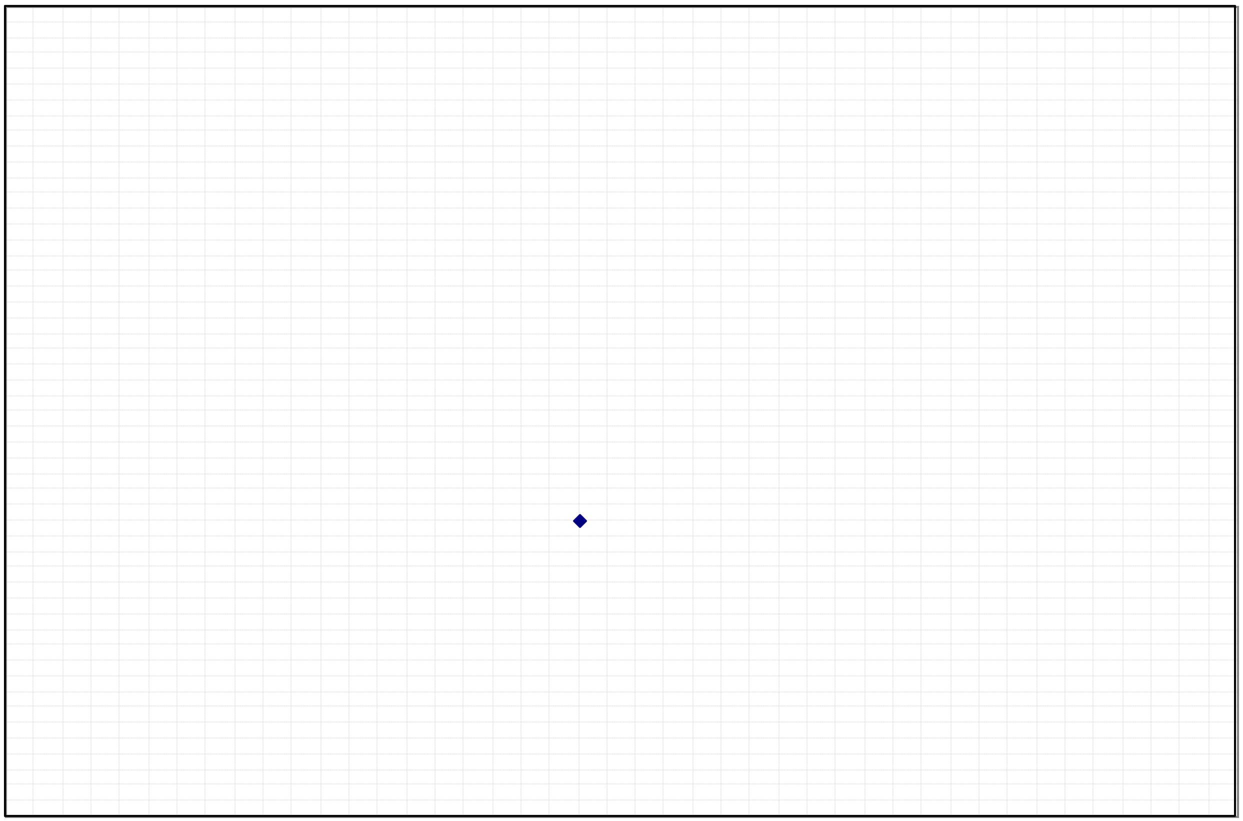
Model Conceptualization



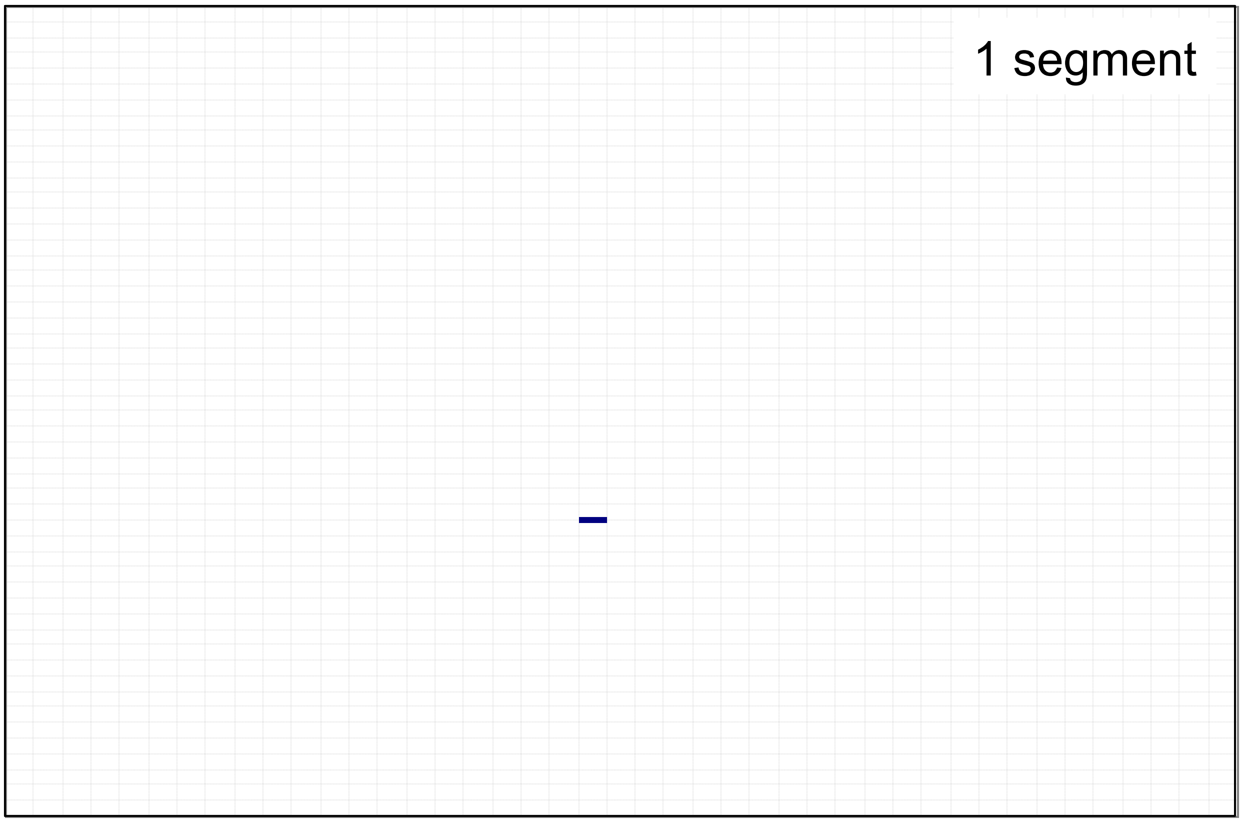
$$\frac{d\varepsilon}{dt} = \dot{\varepsilon}$$

$$N_{De} = \frac{relaxation\ time}{observation\ time} = \frac{\bar{\lambda}}{1/\dot{\varepsilon}} = \bar{\lambda}\,\dot{\varepsilon}$$

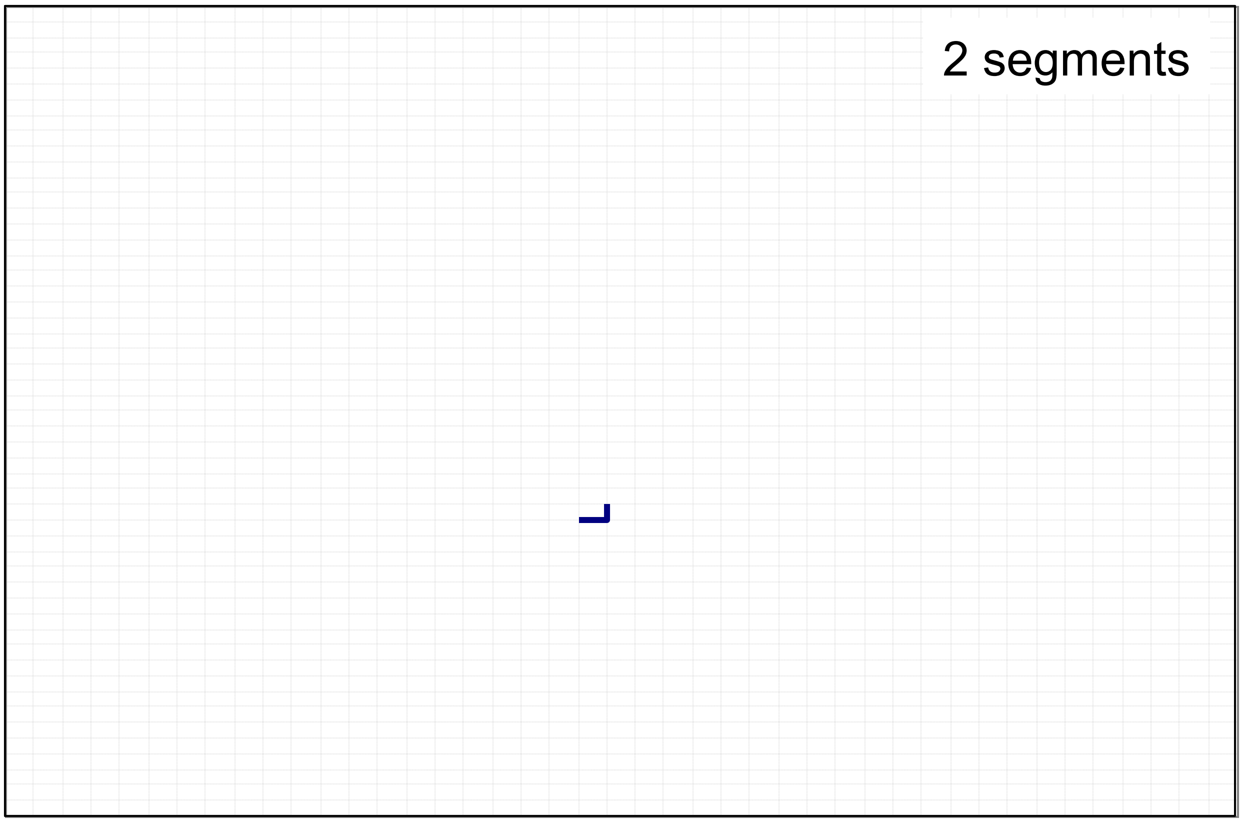
Model Conceptualization



Model Conceptualization



Model Conceptualization



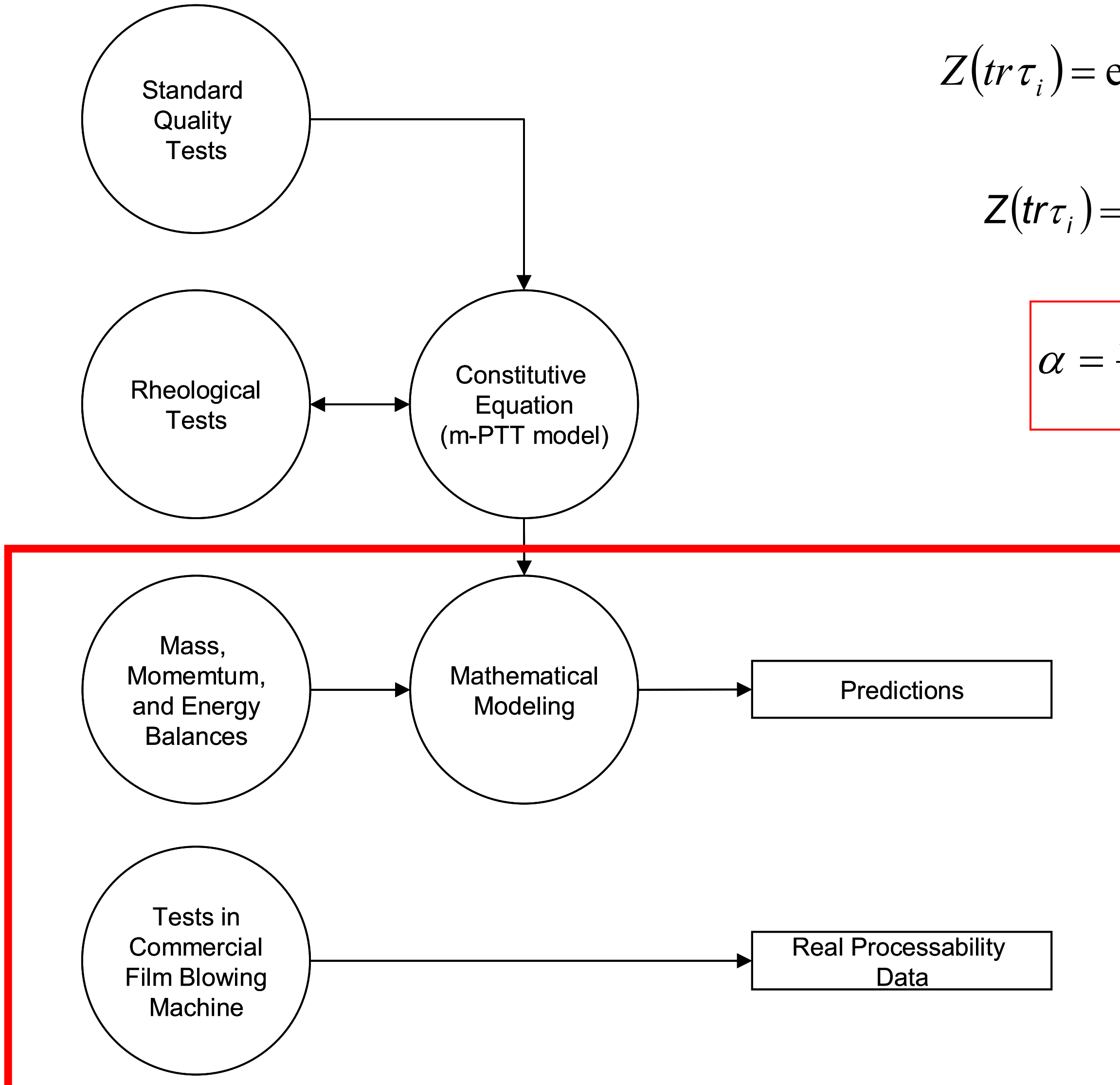
	parameters	comments
Original (Phan Thien and Tanner, 1977)	$\xi = constant$ $\alpha = constant$	• Shear parameter causes violation of Logde-Meissner relationship. • The model fails to predict η_e of s-PP resins. • Larson (1988) and Stephenson (1987) proved that it presents significant limitations.
version 1 (Cortés and Bonilla, 2004)	$\xi = 0$ $\alpha = f(\dot{\varepsilon}, M_z, M_e)$	• According to Larson (1988, 1998) the shear parameter was set to zero. • Using i-PP and s-PP, it was found that α is a function of the extension rate and some MWD parameters
version 2 (Cortés and Bonilla, 2005)	$\xi = 0$ $\alpha = f(\dot{\varepsilon}, M_W)$	• The same study was extended to HDPE and PS. The modified model failed, but it was found that each type of polymer presents a specific function. • An empirical relationship between α and Mw was found. The model allows the prediction of η_e from just Mw and the discrete relaxation spectrum.
version 3 (Cortés and Bonilla, 2006)	$\xi = 0$ $\alpha = f(\dot{\varepsilon}, \bar{\lambda}, \frac{M_e}{M_z}, \frac{M_e}{M_w})$	• In order to obtain a more fundamental model, a deeper analysis to the α parameter was done. • The α parameter was defined as a measurement of the resistance to elongation and is set to be a function of the extension rate, mean relaxation time and the MWD.

$$Z(tr\tau_i)\tau_i + \lambda_i\tau_{i(1)} + \cancel{\frac{\xi}{2}\lambda_i(\dot{\gamma}\cdot\tau_i + \tau_i\cdot\dot{\gamma})} = -\eta_i\dot{\gamma}$$

$$Z(tr\tau_i) = \exp\left(-\frac{\alpha\lambda_i}{\eta_i}tr\tau_i\right)$$

$$Z(tr\tau_i) = \exp\left(-\frac{\alpha}{G_i}tr\tau_i\right)$$

$$\boxed{\alpha = \frac{M_e}{M_z}\ln\left(\dot{\varepsilon}\bar{\lambda}\right) + \frac{M_e}{M_w}}$$



Objective

- *To generate a model that can be used to determine the processability of different materials in the film blowing process using laboratory data (molecular weight distribution and frequency sweep data) and the least possible adjustment parameters.*

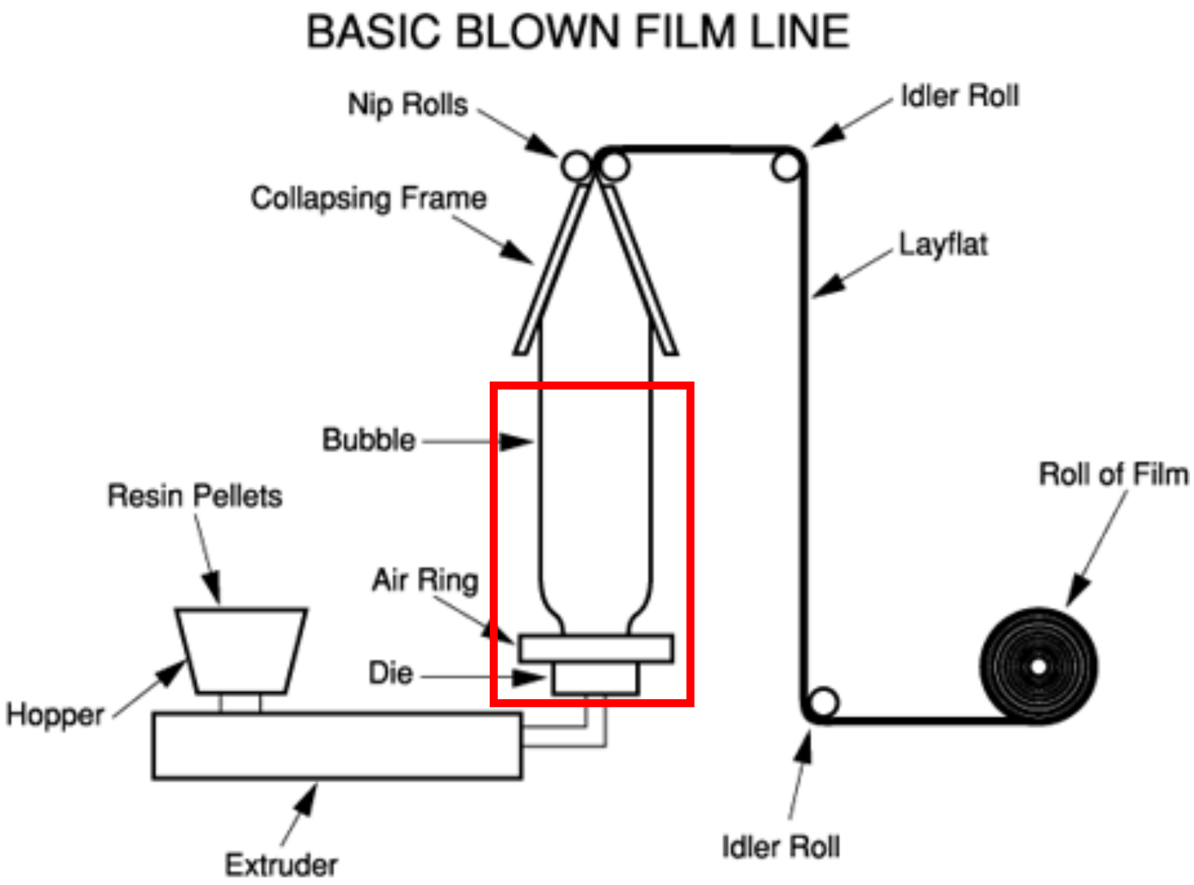
Background

Researchers*	Year	Constitutive Equation	Conditions
Pearson and Petrie	1970	Newtonian	Isothermal
Petrie	1975	Newtonian	Non-isothermal
Han and Park	1975	Power Law	Non-isothermal
Luo and Tanner	1985	Leonov model	Non-isothermal
Cain and Denn	1988	Maxwell and Marruci models	Non-isothermal
Campbell and Cao **	1990	Maxwell and Modified Hookean models	Non-isothermal
Alaie and Papanastasiou	1993	Integral constitutive model	Non-isothermal

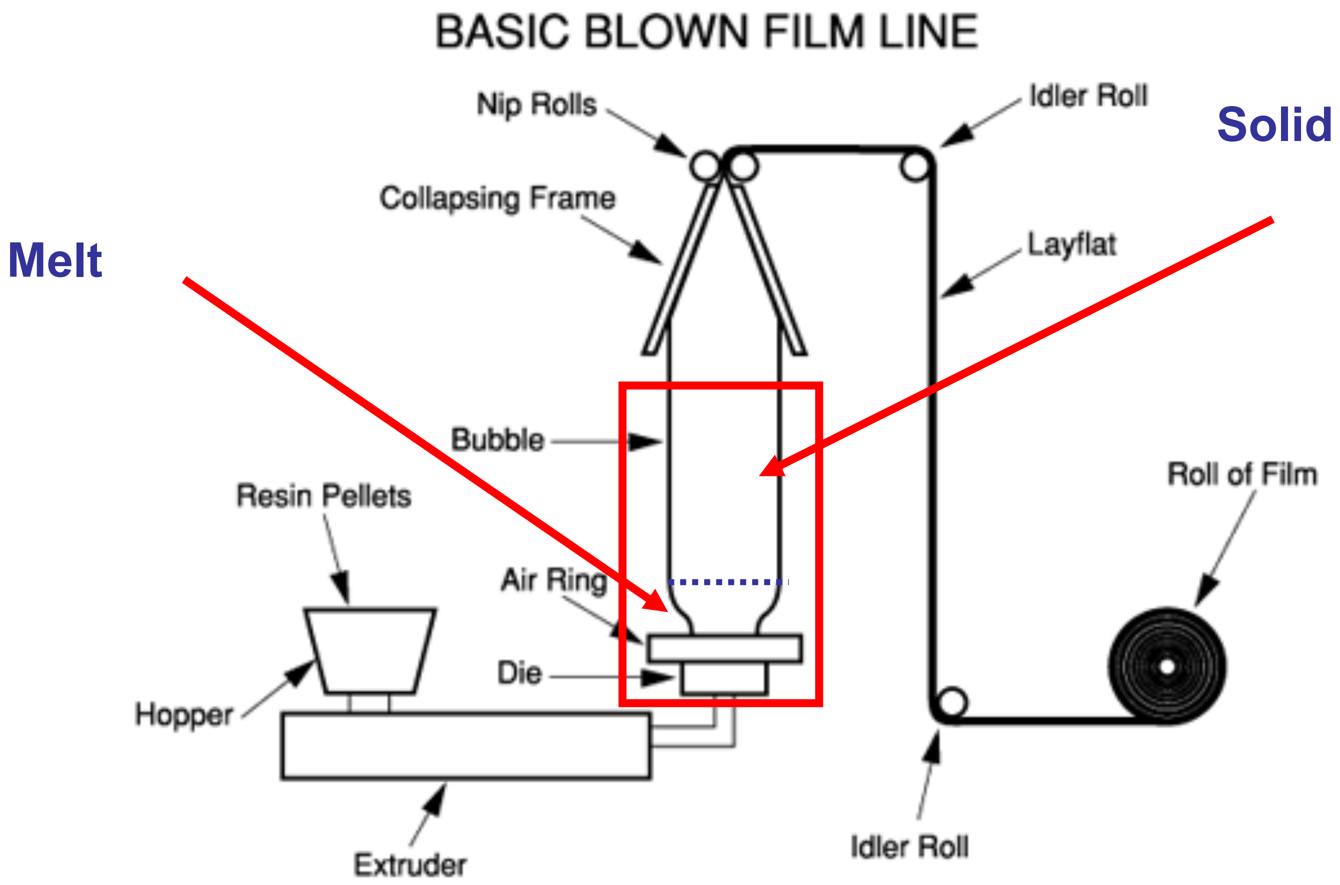
* Most of the researchers used PS experimental data of Gupta *et. al.* (1981) to validate their simulations.

** Campbell and Cao incorporated in their model two phases -liquid-like (below) and solid-like (above the frost line)-

Film Blowing Process

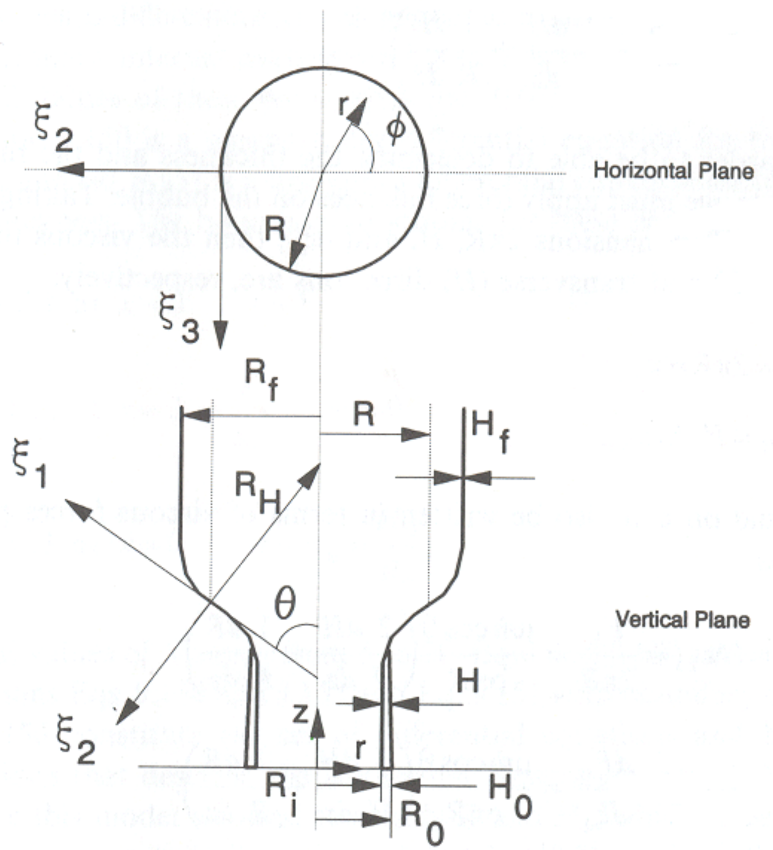


Film Blowing Process

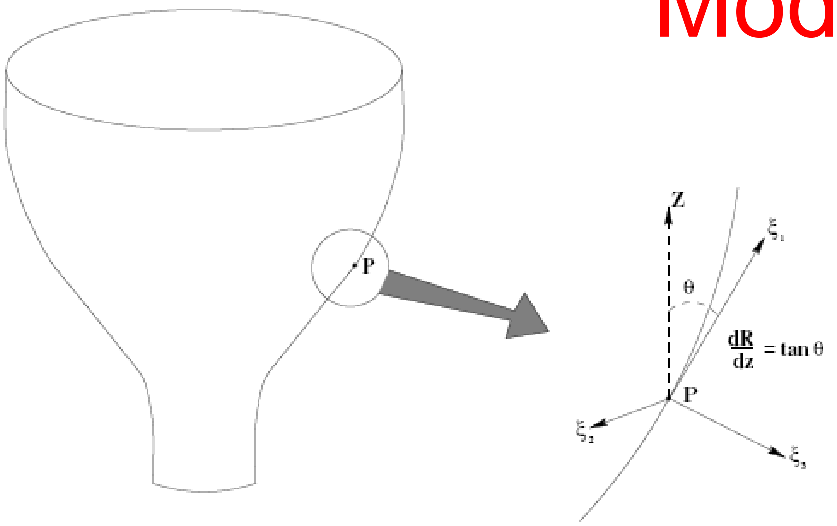


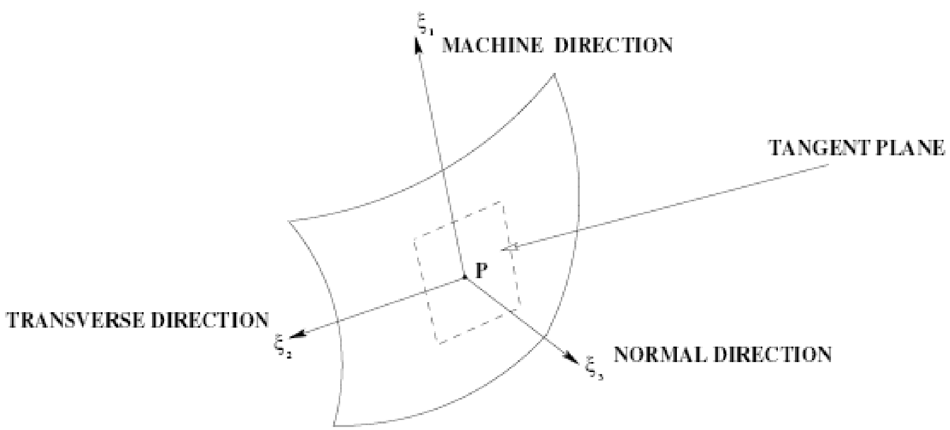
Model

- Symmetry around the z axis is assumed.
- For the calculation of stresses, a moving Cartesian coordinate system, ξ_1, ξ_2, and ξ_3, embedded in the inner surface of the bubble is used.
- The ξ_1 direction is in the direction of the flow, the ξ_2 direction is normal to the film, and the ξ_3 direction is perpendicular to ξ_1 and ξ_2 and tangent to the circumferential directions.



Model





- r Bubble radius
- h Film thickness
- z Axial distance
- T Temperature
- T_a Ambient Temperature
- θ Bubble contour angle
- υ Film velocity
- F_z Take-up speed
- ρ Density
- U Heat transfer coefficient
- C_p Heat capacity
- σ Stefan – Boltzmann constant
- σ_{ii} Total stress component
- ε Emissivity
- m Mass flow

Process Dynamic Equations (Campbell *et. al.*, 1990)

- Deformation rate tensor

$$\dot{\gamma} = \upsilon \cos\theta \begin{bmatrix} \frac{1}{\upsilon}\frac{d\upsilon}{dz} & 0 & 0 \\ 0 & \frac{1}{h}\frac{dh}{dz} & 0 \\ 0 & 0 & \frac{1}{r}\frac{dr}{dz} \end{bmatrix}$$

- Continuity Equation

$$\dot{m} = 2\pi r h \upsilon \rho$$

- Energy Balance

$$\overline{C}_p \frac{\dot{m}\cos\theta}{2\pi R}\frac{dT}{dz} = U\left(T_a - T\right) + \sigma\varepsilon\left(T_a^4 - T^4\right)$$

- Dynamic Analysis *

$$2\pi r h \sigma_{11}\cos\theta - \pi\left(r_f^2 - r^2\right)\Delta P = F_z$$

$$\frac{h\sigma_{11}}{R_L} + \frac{h\sigma_{33}}{R_H} = \Delta P$$

$$R_L = -\frac{\sec^3\theta}{d^2 r / dz^2}$$

$$R_H = r\sec\theta$$

$$\frac{dr}{dz} = \tan\theta$$

* The effects of gravity and surface tension are neglected here (Petrie, 1975)

Constitutive Equation

- The modified PTT (m-PTT) model was used in the liquid-like region.

$$\boldsymbol{\tau} = \sum_{i=1}^{N} \boldsymbol{\tau}_i$$

$$Z(tr\tau_i)\tau_i + \lambda_i \tau_{i(1)} = -\eta_i \dot{\gamma}$$

$$Z(tr\tau_i) = \exp\left(-\frac{\alpha\lambda_i}{\eta_i} tr\tau_i\right)$$

$$\boxed{\alpha = \frac{M_e}{M_z}\ln\left(\dot{\varepsilon}\bar{\lambda}\right) + \frac{M_e}{M_w}}$$

- The solid-like behavior was modeled using a modified Hookean model. (Campbell and Cao, 1990; Doufas, 2000)

The Model

- From process dynamics: 3 differential equations
- From energy balance: 1 differential equation
- From constitutive modeling: 3 differential equations

- Unknowns variables:

r	Bubble radius
h	Film thickness
T	Temperature
p	Thermodynamic pressure
θ	Bubble contour angle
υ	Film velocity
σ_{11}	Stress tensor component
σ_{33}	Stress tensor component

The Model

- From process dynamics: 3 differential equations
- From energy balance: 1 differential equation
- From constitutive modeling: 3 differential equations

$\}$ 7

- Unknowns variables:

$$\dot{m} = 2\pi r h \upsilon \rho$$

$$\upsilon = \frac{\dot{m}}{2\pi r h \rho}$$

r	Bubble radius
h	Film thickness
T	Temperature
p	Thermodynamic pressure
θ	Bubble contour angle
$\boxed{\upsilon}$	$\boxed{\text{Film velocity}}$
σ_{11}	Stress tensor component
σ_{33}	Stress tensor component

$\}$ 7

The Model

INPUT

Initial radius (Die radius)
Initial thickness (Die gap)
Initial contour angle
Temperature @ die
Mass flow
Inflation pressure
Material properties *

Nonisothermal Non-Newtonian Model

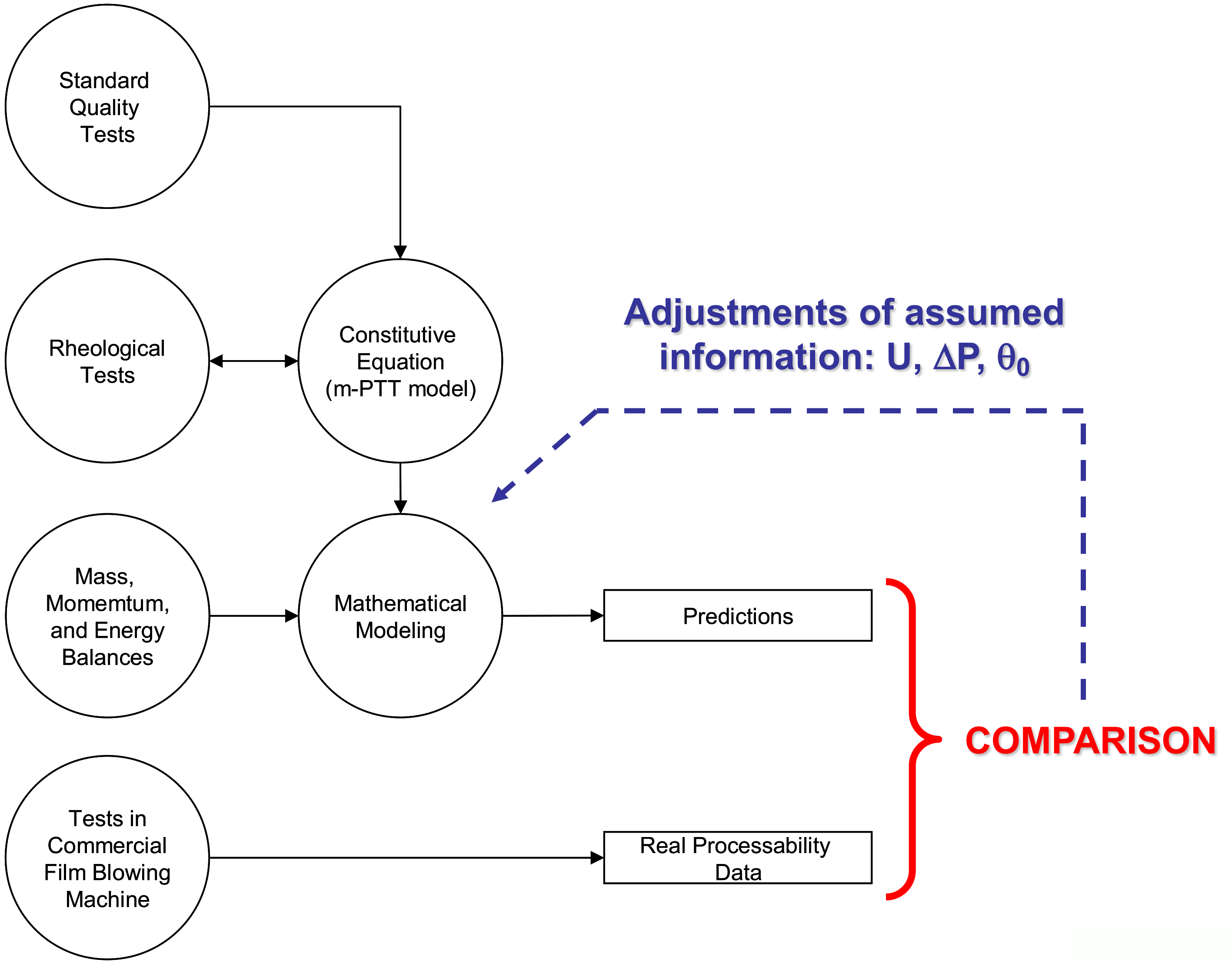
OUTPUT

Bubble radius profile (Bubble shape)

Film thickness profile

Temperature profile

* Material properties include: relaxation spectrum, activation energy, density, heat capacity, heat transfer coefficient, emissivity and MWD averages


Standard Quality Tests
Rheological Tests
Constitutive Equation (m-PTT model)
Adjustments of assumed information: U, ΔP, θ0
Mass, Momemtum, and Energy Balances
Mathematical Modeling
Predictions
COMPARISON
Tests in Commercial Film Blowing Machine
Real Processability Data

Methods

- Determination of parameters needed by the model

Parameter	Determination
Discrete relaxation spectrum	Calculated from frequency sweeps data
MWD averages	Measured by GPC
Activation energy	Calculated from frequency sweeps data @ three different temperatures
Temperature @ die	Measured during the film blowing run
Mass flow	Measured during the film blowing run
Emissivity	Set to thermal camera value (0.96)
Heat capacity	Calculated from DSC experiments
Heat transfer coefficient	Adjusted to fit the bubble radius while blowing
Inflation pressure	Adjusted to fit the bubble radius while blowing
Initial contour angle (θ_0)	Adjusted to fit the bubble radius while blowing

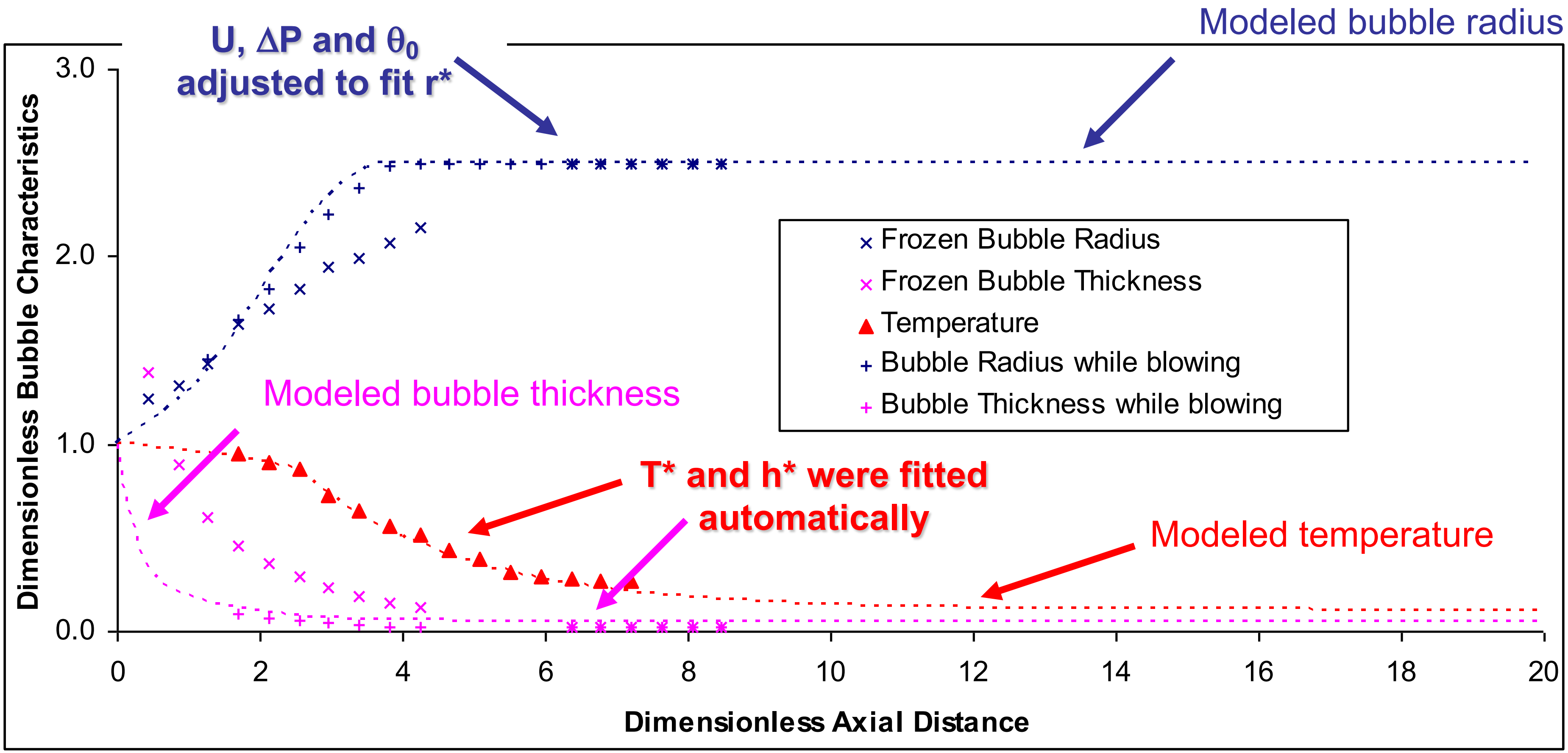
Methods

- Parameters used in the calculations

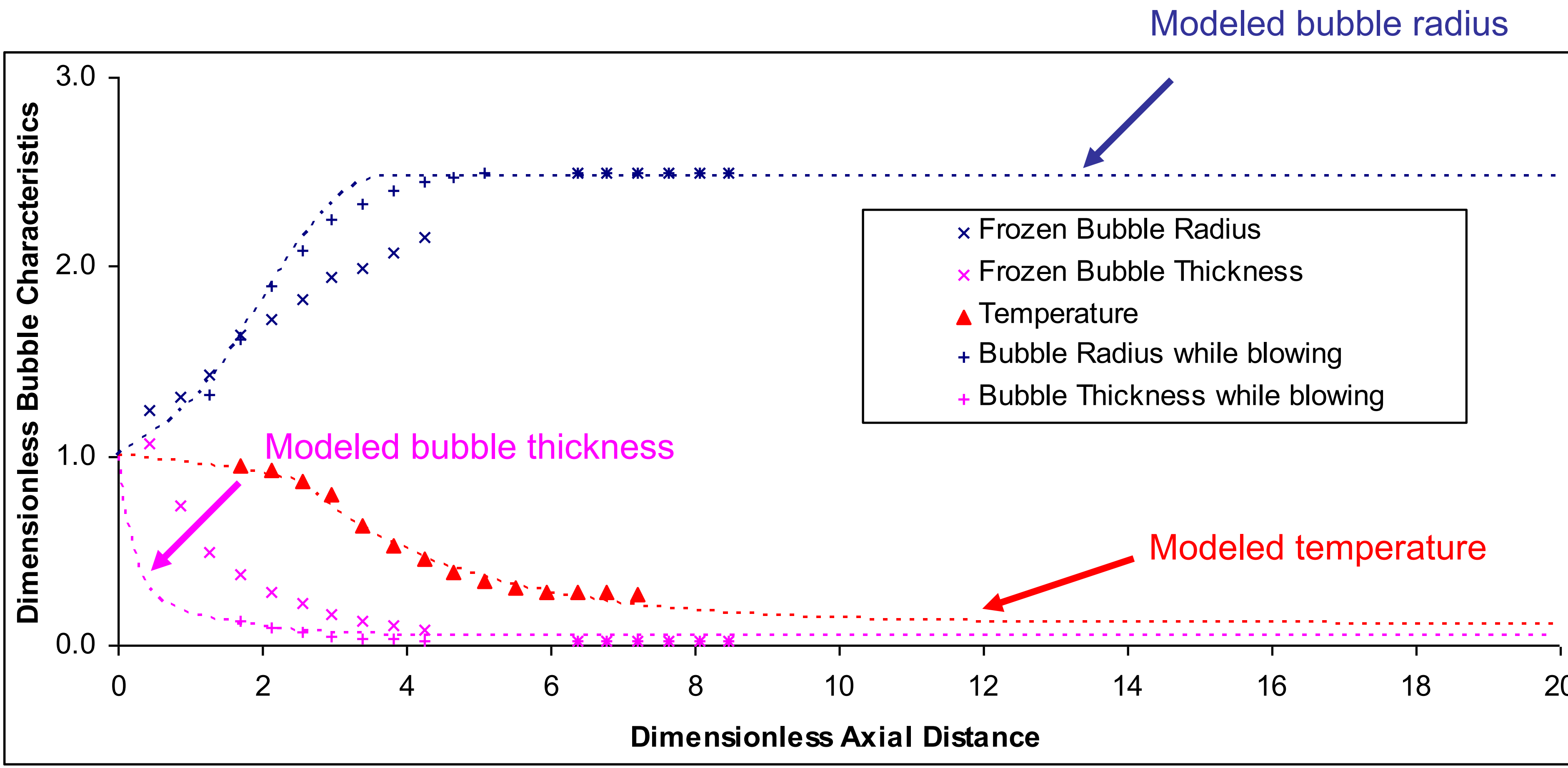
Parameter	I	II	III
Heat transfer coefficient (W/m^2 K) [1]	35	35	35
Emissivity [2]	0.96	0.96	0.96
Inflation pressure (Pa) [3]	228	133	99
Initial contour angle, θ_0 (degrees)	6.88	14.32	22.92

1. Heat transfer coefficient previously used for the film blowing process range from 5 to 50 W/m^2 K (Campbell, 1990, Doufas, 2000)
2. Reported emissivity used for HDPE in the film blowing modeling range from 0.3 to 1 (Campbell, 1990; Baird, 1998; Doufas, 2000)
3. The reported inflation pressure range from 50 to 250 Pa (Campbell, 1990; Baird, 1998, Doufas, 2000; Muslet, 2004)

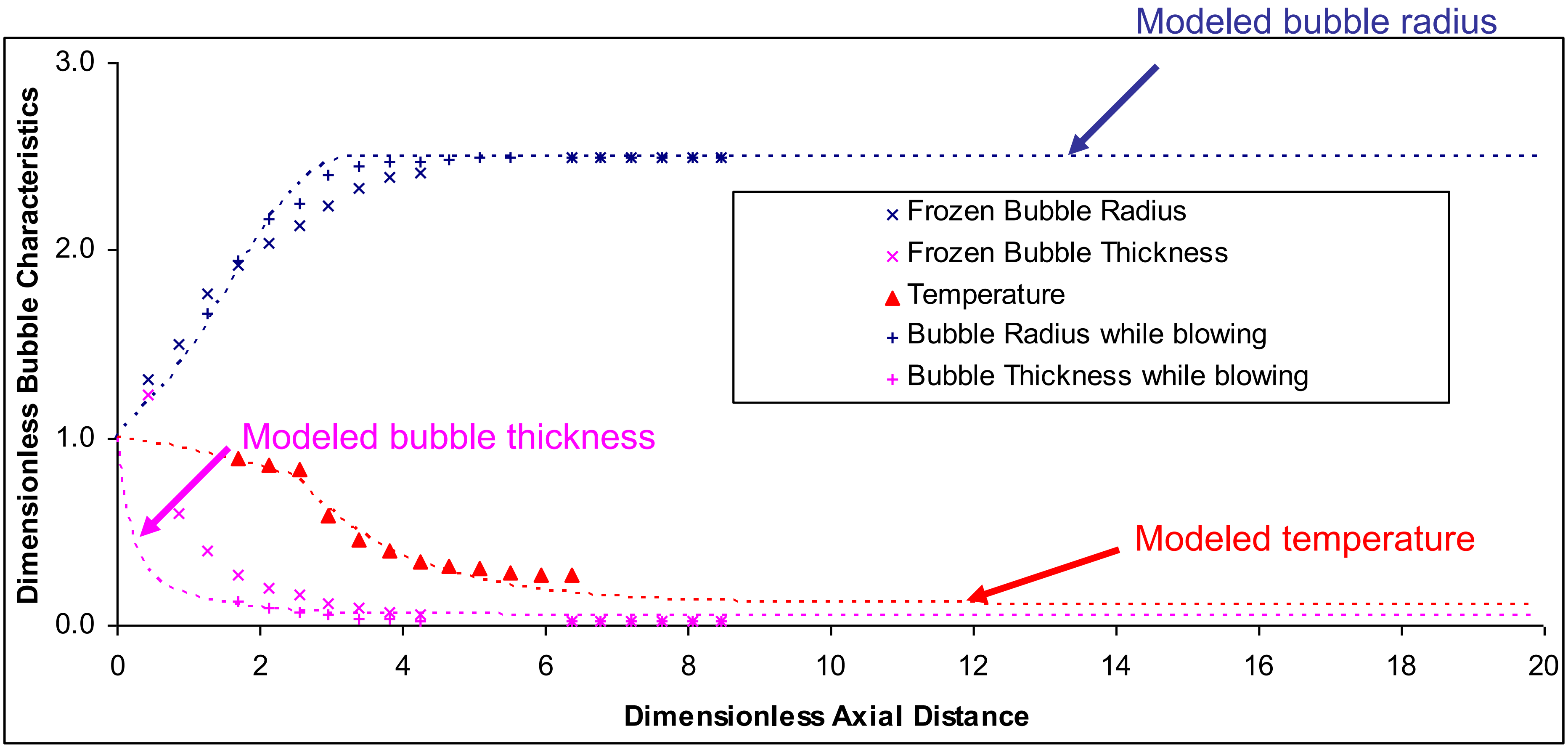
Predictions - I -



Predictions - II -



Predictions - III -



Calculation of θ_0

- Having the actual inflation pressure and heat transfer coefficient might help to calculate the actual θ_0.
- Setting the final (desired) radius, thickness and temperature, θ_0 can be calculated.

Parameter	Proposed Determination Method
Heat transfer coefficient	Estimate it from chemical engineering rules
Inflation pressure	Measure it by a manometer in air inlet

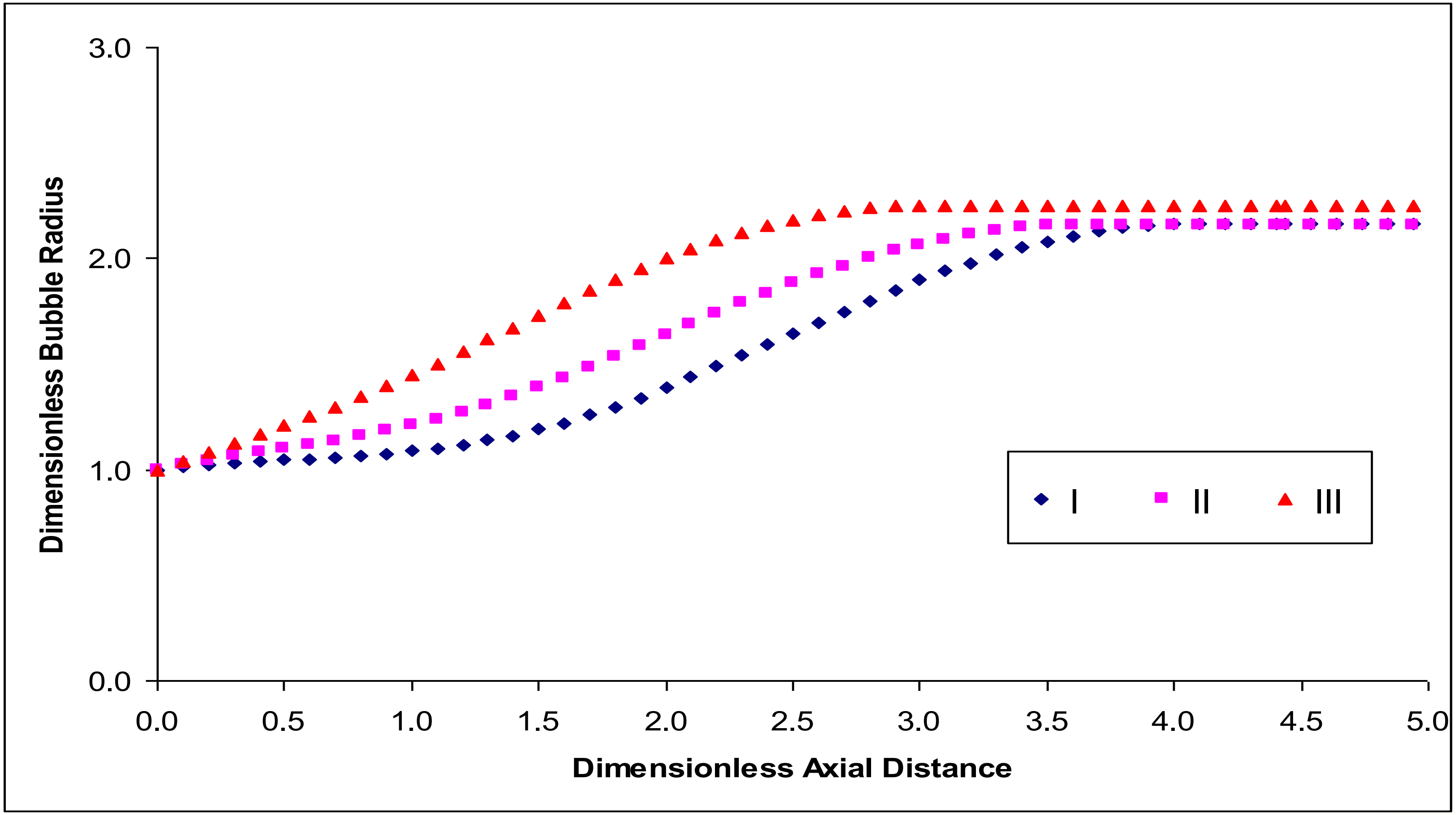
Calculation of θ_0

- Using the same process and product conditions, θ_0 was calculated for the three resins under study.

Parameter	I	II	III
Heat capacity (J/g K)[1]	0.96	1.05	1.098
Heat transfer coefficient (W/m^2 K)[2]	35	35	35
Inflation pressure (Pa)[3]	150	150	150
Mass Flow (g/min)[4]	710	710	710
Final dimensionless radius	2.2	2.2	2.2
Final dimensionless thickness	0.05	0.05	0.05
Final dimensionless temperature	0.15	0.15	0.15
Initial contour angle, θ_0 (degrees)[5]	**4.01**	**15.98**	**28.20**

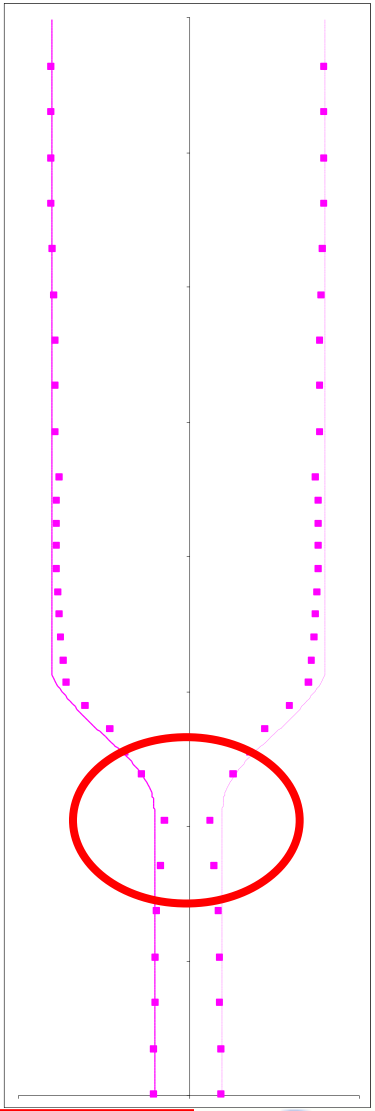
1. Actual heat capacity calculated by DSC experiments.
2. As used in previous calculations.
3. Average of inflation pressures used in previous calculations
4. Average of the experimental data.
5. Calculated from the model. This is the initial contour angle necessary in order to obtained the desired radius, thickness and temperature.

Calculation of θ_0



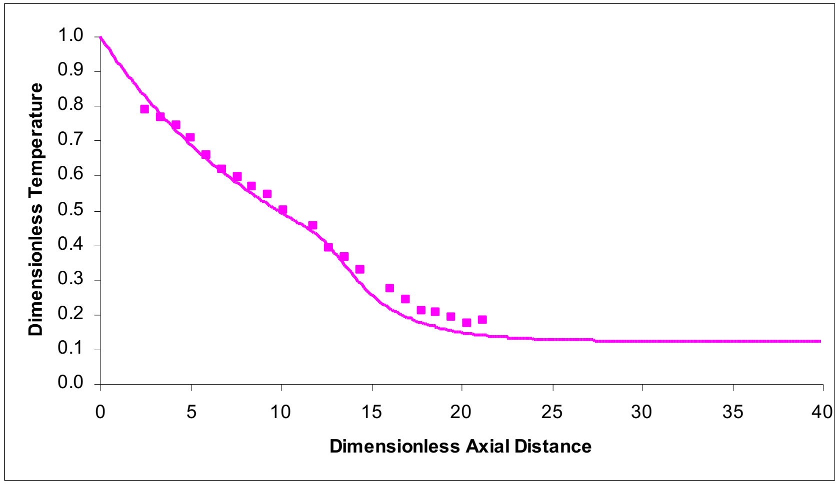
Bimodal resins?

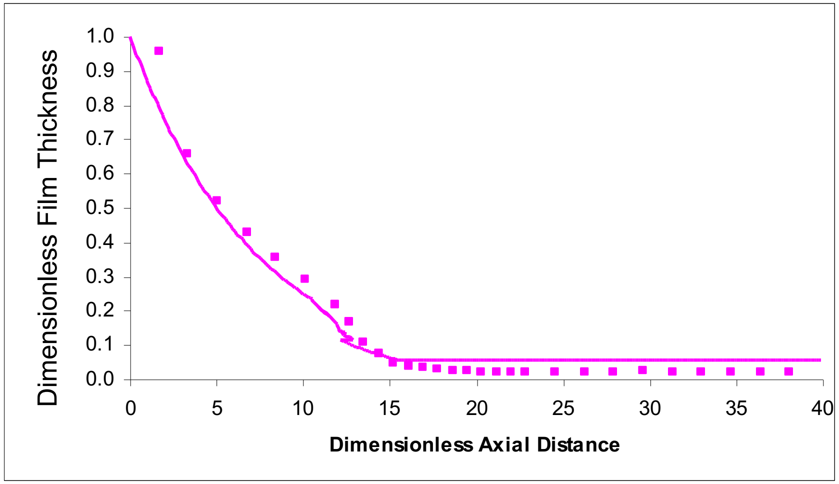
- mPTT model does not predict satisfactorily the elogational viscosity curve (10 to 30% error).
- Nonetheless, the bubble radius profile during the film blowing is fairly well predicted using the proposed model (using the mPTT model as constitutive equation).
- The bubble long neck and the "champagne glass" shape are well predicted; but the "necking" is not.



Bimodal resins

- Predictions of temperature and film thickness profiles are in good agreement to experimental measurements.





Conclusions

- The importance and usefulness of this work lies not only in the capacity of predicting elongational viscosity, but also in the ability of predicting real processability data, all from easily measurable parameters.
- The new m-PTT model proposed allows predicting satisfactorily the elongational viscosity for 31 polyolefins resins from the molecular weight distribution and the discrete relaxation spectrum.
- A non-isothermal model able of predicting the processability of different materials in the film blowing process using laboratory data (molecular weight distribution and frequency sweep data) was generated.

Potential Benefits

- The characterization of new materials.
- The tailoring of new materials with specific rheological and end product properties.
- The benchmarking of resins with specific applications.
- The simulation of polymer processing and consequently for savings of time and money devoted to semi-industrial and/or application lab trials.
- The identification of material parameters that can be related to processability parameters (such as die swell, bubble stability, melt fracture, etc.).
- The development of a user friendly software helping in the decision making for the tech service and R&D departments.
- And the increasing of the general knowledge of the rheological behavior of polymers.

Potential Benefits

- Support the ability to produce totally new materials with technological innovation at efficient production rates.
- Increase the knowledge of the film blowing process by means of quantitative engineering analyses.
- Establish the processability of new polymers.
- Predict the material parameters from processing behavior.
- Establish a relationship between molecular weight features and final film properties.
- Select materials for a given equipment and final product properties.
- Design equipment for a given material and final product properties.