2.882

Chapter 8 of Complexity

Reduction of Complexity in Materials through Functional Periodicity

Functional Periodicity related to materials found in Nature

- Periodic Table of chemical elements
- Crystalline solids
- Atomic structure (electrons in valence bands)
- Biological systems

Engineered Materials

- **Functional Periodicity to to prevent unstable crack growth**

- ***Wire rope***
- ***Fabric***
- ***Composites***

Crack Growth

- **Unstable crack growth**

$$k_1 = \sigma_{22\infty}\sqrt{c}$$

Figure removed for copyright reasons.
See Figure 8.1 in [Complexity]:
Suh, N. P. *Complexity: Theory and Applications*. New York, NY: Oxford University Press, 2005. ISBN: 0195178769.

Crack Growth

- **Fatigue crack growth under cyclic loading**

$$\frac{dc}{dN} = A\left(\frac{\Delta k_1}{\sigma_Y}\right)^n$$

Figure removed for copyright reasons.
See Figure 8.2 in [Complexity].

Composites

-

Figure removed for copyright reasons.
See Figure 8.3 in [Complexity].

Functional Periodicity for Control of Material Properties

Edge and Screw Dislocations

Figure removed for copyright reasons.
See Figure 8.4 in [Complexity].

Functional Periodicity for Control of Material Properties

Stress-Strain Relationship showing work-hardening

Figure removed for copyright reasons.
See Figure 8.5 in [Complexity].

Functional Periodicity for Control of Material Properties

Annealing to eliminate dislocations

Figure removed for copyright reasons.
See Figure 8.6 in [Complexity].

Functional Periodicity for Control of Material Properties

Wire Drawing

Figure removed for copyright reasons.
See Figure 8.7 in [Complexity].

Microcellular Plastics
(Distortion of injection molded parts)

Request of Our Research Sponsor
Eastman Kodak (Gordon Brown)

- Provide a means of reducing the consumption of plastics
  - Maintaining the same toughness of plastics and the same geometric shape

The “customer needs” may be stated in terms of the following FRs and Cs:

Functional Requirements:

FR1 = Reduce consumption of plastics

FR2 = Maintain the toughness of parts

Constraint:

The shape of products must remain the same.

Design of Microcellular Plastics

The highest level FRs

FR1 = Reduce the amount of plastic used

FR2 = Increase the toughness of the plastic product

FR3 = Make three-dimensional geometrical shape

Design of Microcellular Plastics

Conceptual Solution

A large number of microscale bubbles

Design of Microcellular Plastics

The highest level FRs

FR1 = Reduce the amount of plastic used

FR2 = Increase the toughness of the plastic product

FR3 = Make three-dimensional geometrical shape

The corresponding highest level design parameters (DPs) are:

DP1 = Number of cells

DP2 = Cell size

DP3 = Die or mold design

Design of Microcellular Plastics

The design equation for the product:

$$\begin{Bmatrix} FR1 \\ FR2 \\ FR3 \end{Bmatrix} = \begin{bmatrix} X & X & 0 \\ 0 & X & 0 \\ 0 & 0 & X \end{bmatrix} \begin{Bmatrix} DP1 \\ DP2 \\ DP3 \end{Bmatrix}$$

What is a Microcellular Plastic?

Microcellular Plastics (MCP) is defined as the plastic that has a large number of small bubbles, typically less than 30 microns.

What is a Microcellular Plastic?

Cell Size (μm)	Cell Density (Cells/ cm^3)
0.1	10^{15}
1	10^{12}
10	10^{9}

Morphology of MuCell

Photo removed for copyright reasons.

Polystyrene Products

Photo removed for copyright reasons.

PP Products

Photo removed for copyright reasons.

Photo removed for copyright reasons.

PVC profiles

Injection Molded Printer Chassis

Photo removed for copyright reasons.

Injection Molding of Microcellular Plastics vs Solid Plastics

TRW -- Air bag Canister (Material: 33% glass filled Nylon)

	Solid	MuCell	% red.
Part weight	365 gms	252 gms	31%
Cycle time	45 sec	35 sec	22%
Tonnage	150 tons	15 tons	90%

» (Courtesy of Mar Lee Companies)

Advantages of Microcellular Plastics

- Reduction of material consumption (from 5 to 95 %)
- Faster cycle time
- Higher productivity
- Greater toughness in some plastics
- Dimensional accuracy
- Dimensional stability
- No warping

Advantages of Microcellular Plastics

- Appearance (no visible cells)
- Thin sections
- No sink marks
- Low temperature process
- Low pressure process
- Large number of cavities or smaller machines
- Most polymers

Advantages of Microcellular Plastics

- Use of non-hydrocarbon solvents -- CO_2 and N_2
- No additives for nucleation
- No reactive components such as viscosity modifiers
- No special equipment other than gas supply system -- similar conventional machines

Question: What is the physical basis for MuCell technology?

***Simultaneous* nucleation**

of an *extremely* large number of cells!!

How do we achieve *the simultaneous* nucleation of an *extremely* large number of cells?

Design of the Process Technique for Microcellular Plastics

(The first student to work on the batch process --
Jane Martini, SM Thesis, MIT)

The processing technique consists of dissolving a large amount of gas to form *polymer/gas solution* and then inducing sudden *thermodynamic instability* by either lowering the pressure or raising the temperature to change the solubility of the gas.

Sudden Change in Solubility

- The solubility is a function of two thermodynamic properties, temperature and pressure:

$$S = S(p, T)$$

- The change in the solubility can be expressed as:

$$\Delta S = \frac{\partial S}{\partial p} \Delta p + \frac{\partial S}{\partial T} \Delta T$$

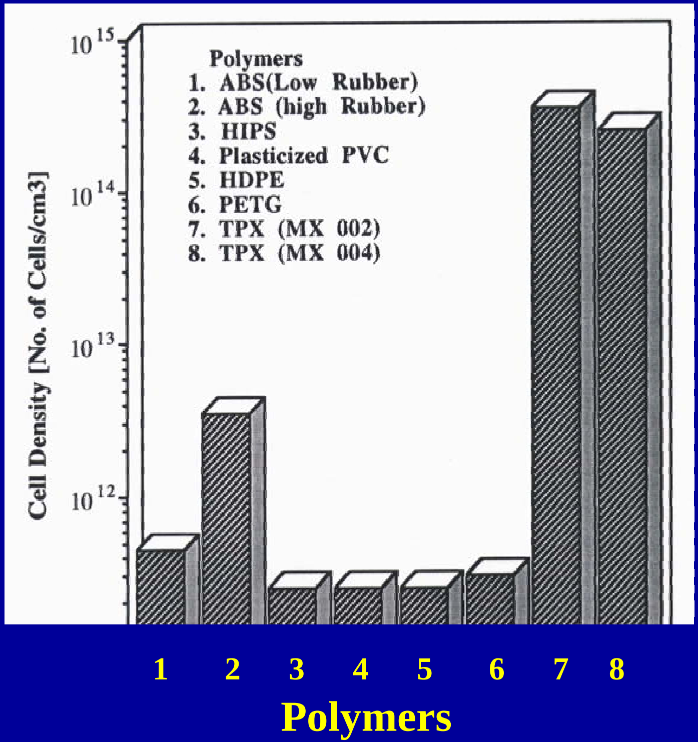
Microcellular Plastics by Batch Process

(From Cha, Ph.D.Thesis, MIT)

Cell sizes of the microcellular foamed polymers (Ambient temperature foaming). Note: Saturation pressure and temperature of CO_s were not the same for all polymers.

Microcellular Plastics by Batch Process

(From Cha, Ph.D.Thesis, MIT)



Cell density of the microcellular foamed polymers (Ambient temperature foaming). Note: Saturation pressure and temperature of CO_s were not the same for all polymers.

What is the basic physics behind continuous processes?

Microcellular Plastics
- Design of a Continuous Process

To create a continuous process, we must be able to design a process and associated equipment to perform following four functions:

(1) Rapid dissolution of gas into molten, flowing polymer to form a solution,

(2) Nucleation of a large number of cells,

(3) Control of the cell size, and

(4) Control of the geometry of the final product.

Microcellular Plastics
- Design of a Continuous Process

Extruder

(1) Rapid dissolution of gas into molten, flowing polymer to form a solution,

Die/Mold

(2) Nucleation of a large number of cells,

(3) Control of the cell size, and

(4) Control of the geometry of the final product.

Physics of the Continuous Process

1. Polymer/Gas Solution in Extruders

Important Parameters for Formation of Polymer/Gas Solution:

1. Temperature
2. Pressure
3. Degree of mixing of gas and polymer

Introduction to Physics of the Continuous Process

i. Gas diffusion and formation of polymer/gas solution

$$\boxed{t \propto \frac{\ell^2}{\alpha}}$$

Brief Introduction to Physics of the Continuous Process

Polymer	D of CO_2 (cm^2/s)		D of N_2 (cm^2/s)	
	At 188 C	At 200 C	At 188 C	At 200 C
PS	--	$1.3x10^{-5}$	--	$1.5x10^{-5}$
PP	$4.2x10^{-5}$	--	$3.5x10^{-5}$	--
PE	--	$2.6x10^{-6}$	--	$8.8x10^{-7}$
HDPE	$5.7x10^{-5}$	$2.4x10^{-5}$	$6.0x10^{-5}$	$2.5x10^{-5}$
LDPE	--	$1.1x10^{-4}$	--	$1.5x10^{-4}$
PTFE	--	$7.0x10^{-6}$	--	$8.3x10^{-6}$
PVC	--	$3.8x10^{-5}$	--	$4.3x10^{-5}$

Table 7.1 Estimated diffusion coefficients of gases in polymers at elevated temperatures (From Durril, P. L., Griskey, R. G., AIChE Journal, Vol. 12, p 1147 (1960 and Vol. 15, p 106 (1969)

Brief Introduction to Physics of the Continuous Process

Table 7.2 Estimated diffusion time at various striation thickness and diffusion coefficients. (From Park 1996)

Brief Introduction to Physics of the Continuous Process

Figure removed for copyright reasons.

Deformation of a spherical bubble in a shear field to form an ellipsoid. The distance between the ellipsoids (measured perpendicular to the major axis of the ellipsoids) is the striation thickness. The dissolution rate of gas increases as the striation thickness becomes smaller and as the interfacial area of gas/polymer increases.

Physics of the Continuous Process

Gas solubility

Polymer	CO_2 weight gain (%)	N_2 Weight gain (%)
PE	14	3
PP	11	4
PS	11	2
PMMA	13	1

Table 7.3 Estimated gas solubility in polymers at 200°C and 27.6 MPa (4,000 psi) (Park, 1993).

How high should the pressure be in the extruder or the plasticating section of the injection molding machine?

How high should the pressure be in the extruder or the plasticating section of the injection molding machine?

Pressure should be high enough to prevent the formation of two phase throughout the system until ready for cell nucleation.

Physics of the Continuous Process

2. Nucleation of Cells

Physics of the Continuous Process

Classical Nucleation Theory

Free energy change due to the formation of bubbles

$$\Delta G = \Delta G_v + \Delta G_s$$

Critical cluster is formed when

$$\frac{\mathrm{d}}{\mathrm{dr}}(\Delta G) = 0$$

Physics of the Continuous Process

Classical Nucleation Theory

(From Sanyal, Ph.D.Thesis, MIT)

Nucleation rate

$$\frac{\mathrm{dN}}{\mathrm{dt}} = J = N_0 f \exp\left[-\frac{16}{3kT}\pi\sigma^3\left\{\frac{RT}{P_g A^*\left(zU(1-2\xi) + kT\ln\left(\frac{\xi}{1-\xi}\right)\right) + RT\ln\frac{P_g}{P}}\right\}\right]$$

Nucleation Theory

Nucleation rate:

$$\frac{dN}{dt} = N_0 \lambda \exp\left(\frac{-[\Delta G - \Delta G^*(\text{gas concentration})]}{kT} \right)$$

ΔG = Activation energy barrier

$= f(\text{ impurities, mol.orientation, etc.})$

ΔG^* = Energy change due to supersaturation of gas

Possible Nucleation Sites and ΔG

(Approximately Lowest to Highest)

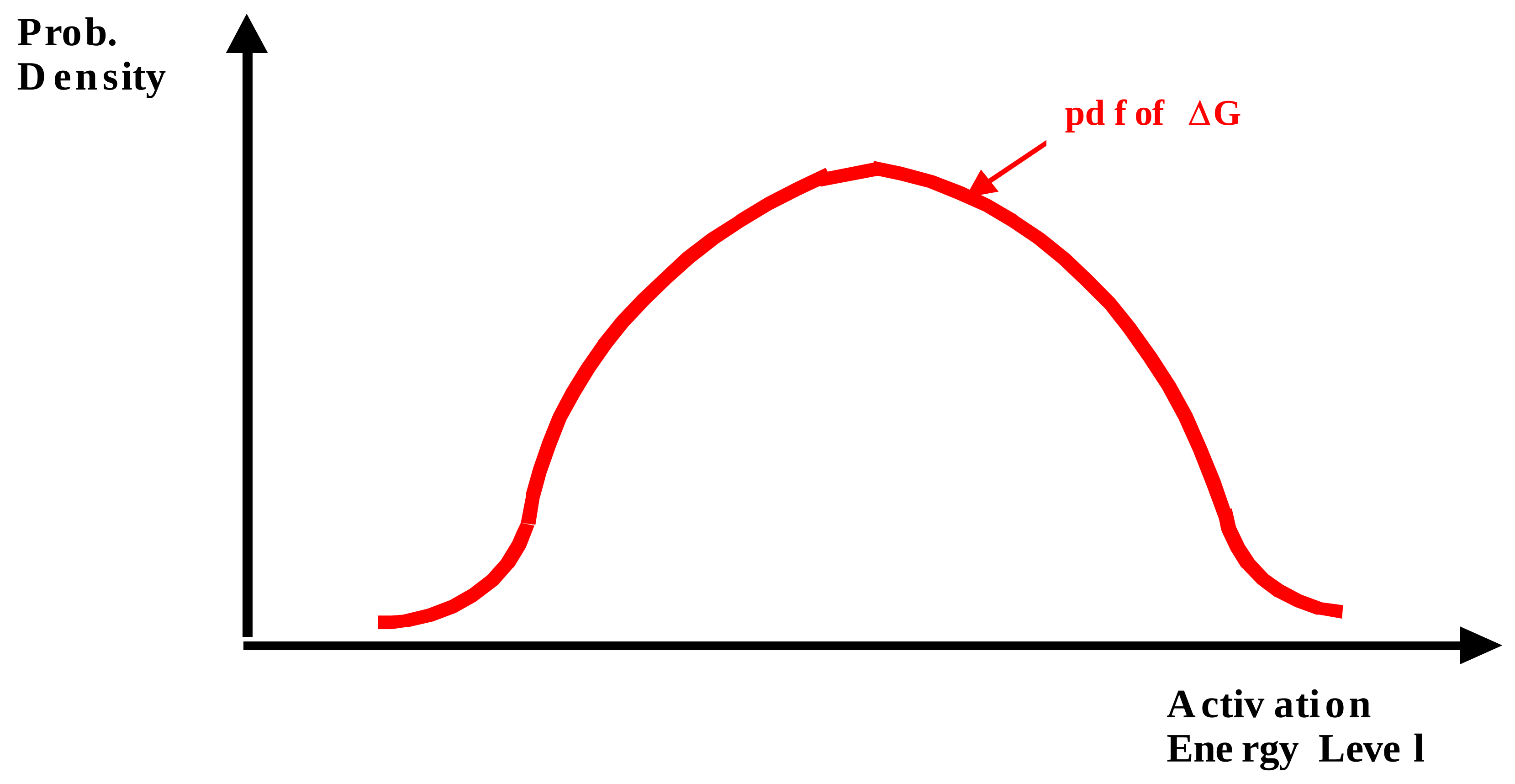
- Solid/polymer interface (heterogeneous nucl.)
- Non-polar polymer/polar polymer interface
- High strain region
- Free volume
- Crystalline/amorphous interface in a polymer
- Interface between crystallites
- Morphological defects in a polymer
- Polar groups of polymers

Possible Nucleation Sites and ΔG

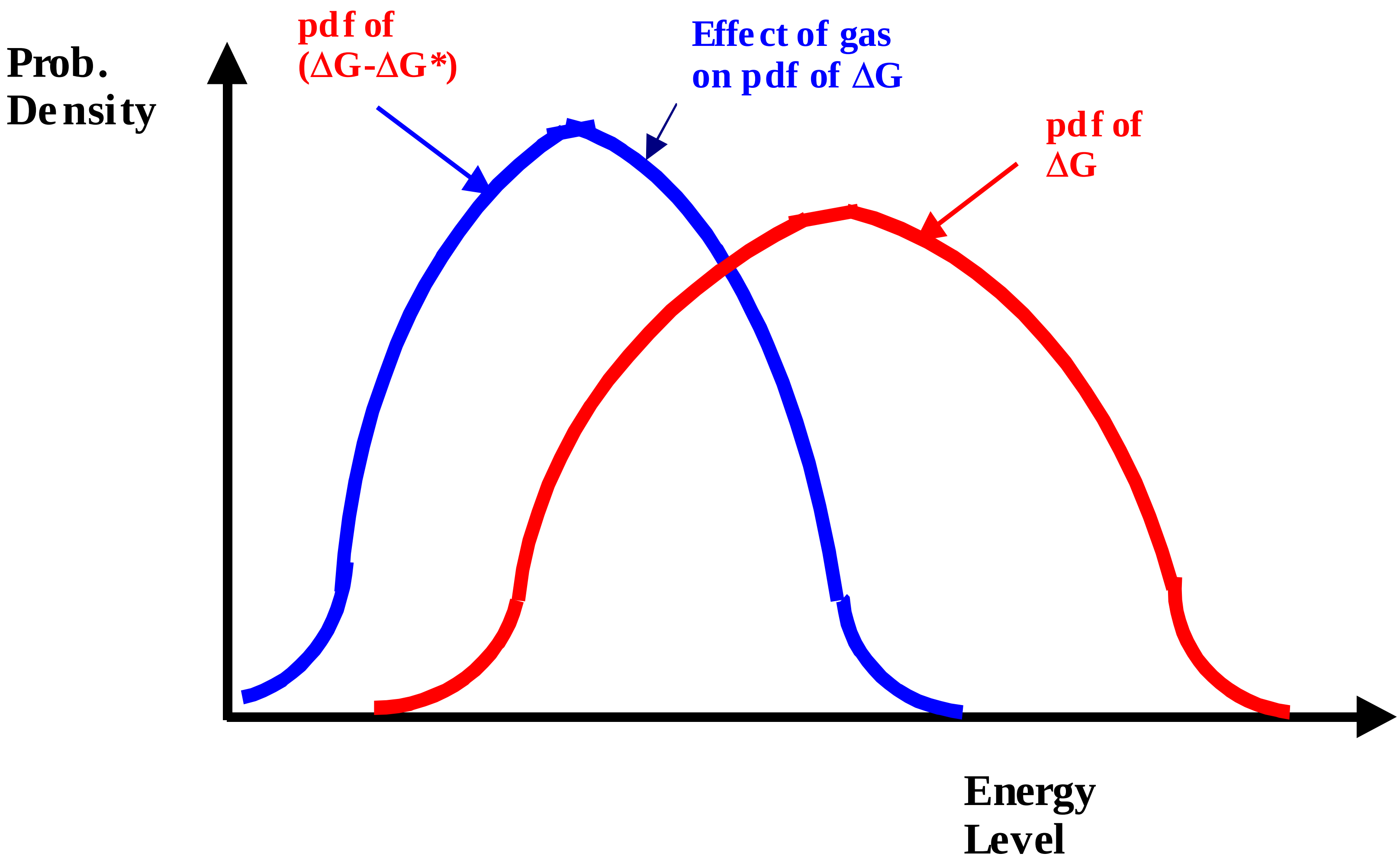
(Approximately Lowest to Highest)

Potential sites	Rough estimation of potential number of nucleation sites (??)
Solid/polymer interface	10^5 to 10^6 /cc
Non-polar polymer/polar polymer interface	---
High strain region	---
Free volume	10^9 /cc
Crystalline/amorphous interface in a polymer	10^{12}/cc
Interface between crystallites	10^{18} /cc
Morphological defects in a polymer	---
Polar groups of polymers	10^{22} /cc

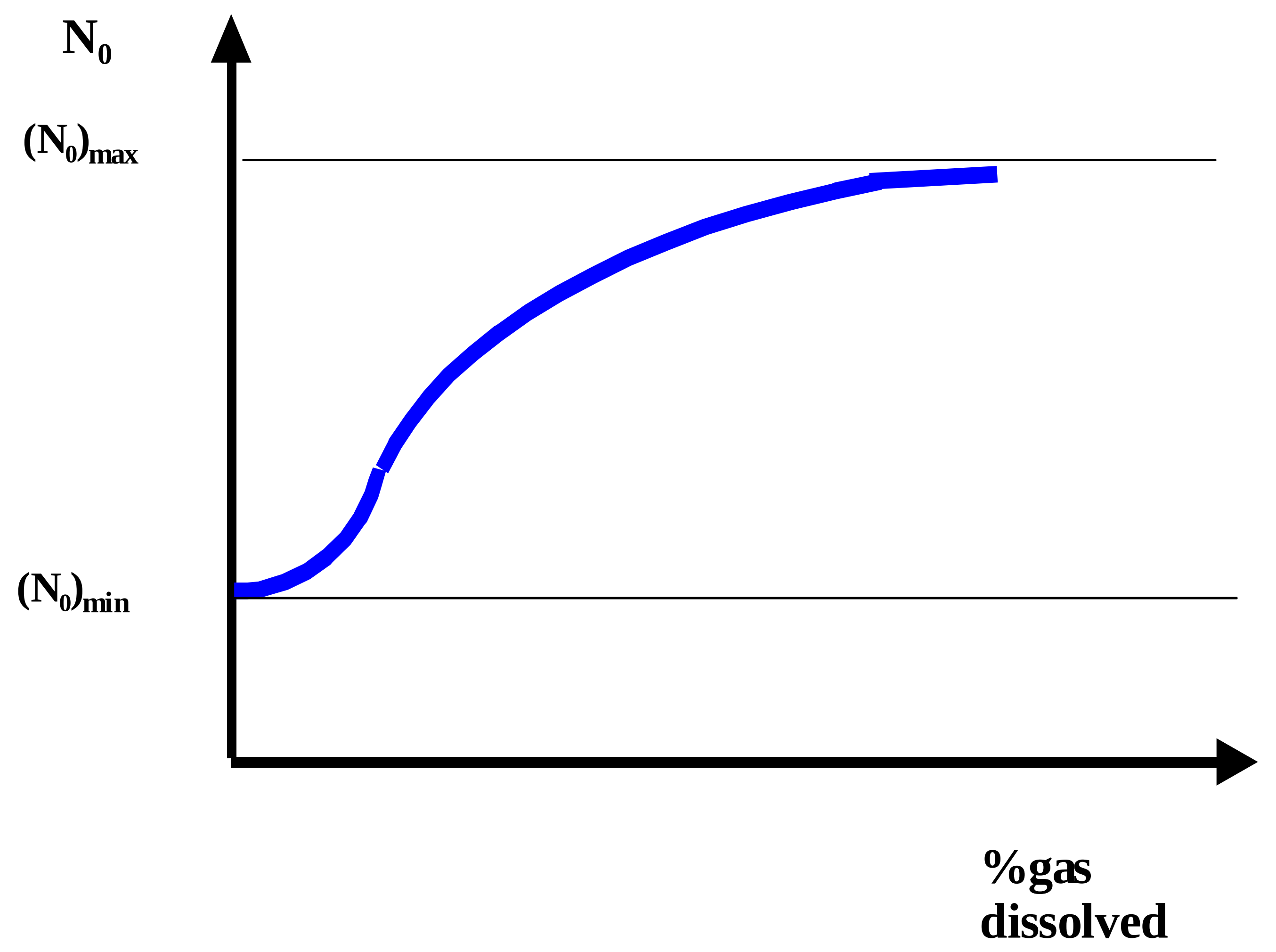
Probability Distribution of Activation Energy



Effect of Gas on the Probability Density of Activation Energy



N_0 as a function of % gas dissolved



How do we achieve *the simultaneous* nucleation of an *extremely* large number of cells?

Answer #1:

By creating a large driving force that can easily overcome all *activation energy barriers* for nucleation

How do we achieve *the simultaneous* nucleation of an *extremely* large number of cells?

Answer #2:

By making sure that the nucleation rate is faster than the diffusion rate.

Nucleation Theory

Condition for Simultaneous Nucleation:

(From Baldwin, Ph.D.Thesis, MIT)

$$\frac{\text{Characteristic nucleation time}}{\text{Characteristic diffusion time}} << 1$$

$$\frac{\alpha}{\frac{dN}{dt} d_c} << 1$$

Nucleation Theory

Condition for Simultaneous Nucleation:

(From Baldwin, Ph.D.Thesis, MIT)

$$\frac{\text{Characteristic gas diffusion distance}}{\text{Characteristic spacing between stable nuclei}} << 1$$

$$2\rho_c^{1/3}(\alpha\, t_D)^{1/2} << 1$$

How do we achieve *the simultaneous* nucleation of an *extremely* large number of cells?

Answers:

1. **By creating a large driving force**

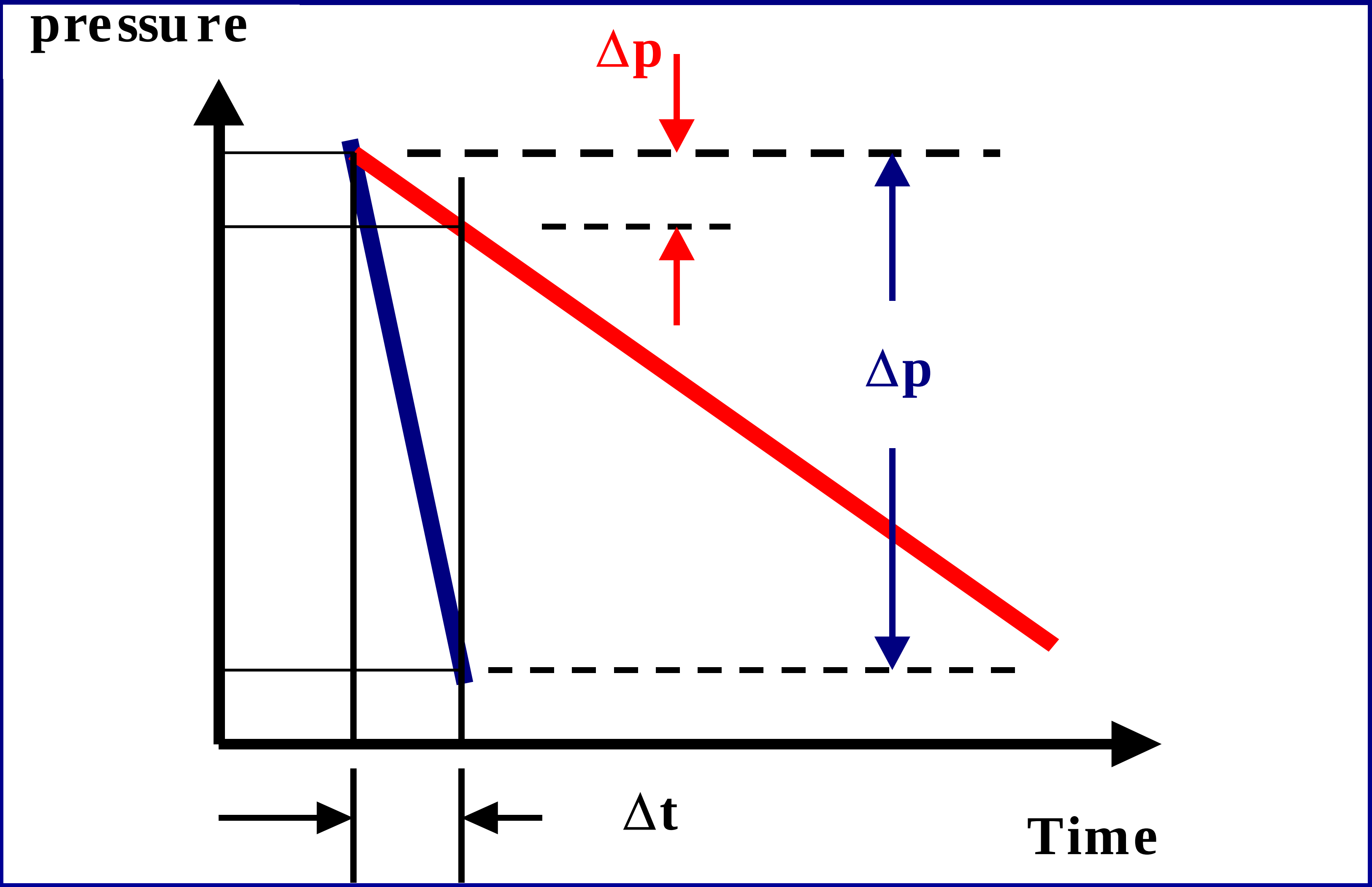
2. **By making sure that the nucleation rate is faster than the diffusion rate.**

How can we make the nucleation time as short as possible and the driving force as large as possible?

How can we make the nucleation time as short as possible and make the driving force as large as possible?

1. Make $(-dp/dt)$ large

Why do we need to make (-*dp/dt*) *large*?



How large should dp/dt be?

How large should dp/dt be?

Answer

It depends on the following:

(1) the temperature of the plastic
(2) materials
(3) die or mold design

How large should dp/dt be?

Polymer	D of CO_2 (cm^2/s)		D of N_2 (cm^2/s)	
	@ 188	@ 200 C	@ 188 C	@ 200 C
PS	--	$1.3x10^{-5}$	--	$1.5x10^{-5}$
PE	--	$2.6x10^{-6}$	--	$8.8x10^{-7}$
HDPE	$5.7x10^{-5}$	$2.4x10^{-5}$	$6.0x10^{-5}$	$2.5x10^{-5}$
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PTFE	--	$7.0x10^{-6}$	--	$8.3x10^{-6}$
PVC	--	$3.8x10^{-5}$	--	$4.3x10^{-5}$
PP	$4.2x10^{-5}$	--	$3.5x10^{-5}$	--

Table 7.1 Estimated diffusion coefficients of gases in polymers at elevated temperatures (From Durril, P. L., Griskey, R. G., AIChE Journal, Vol. 12, p 1147 (1960 and Vol. 15, p 106 (1969)

How large should (*-dp/dt*) be?

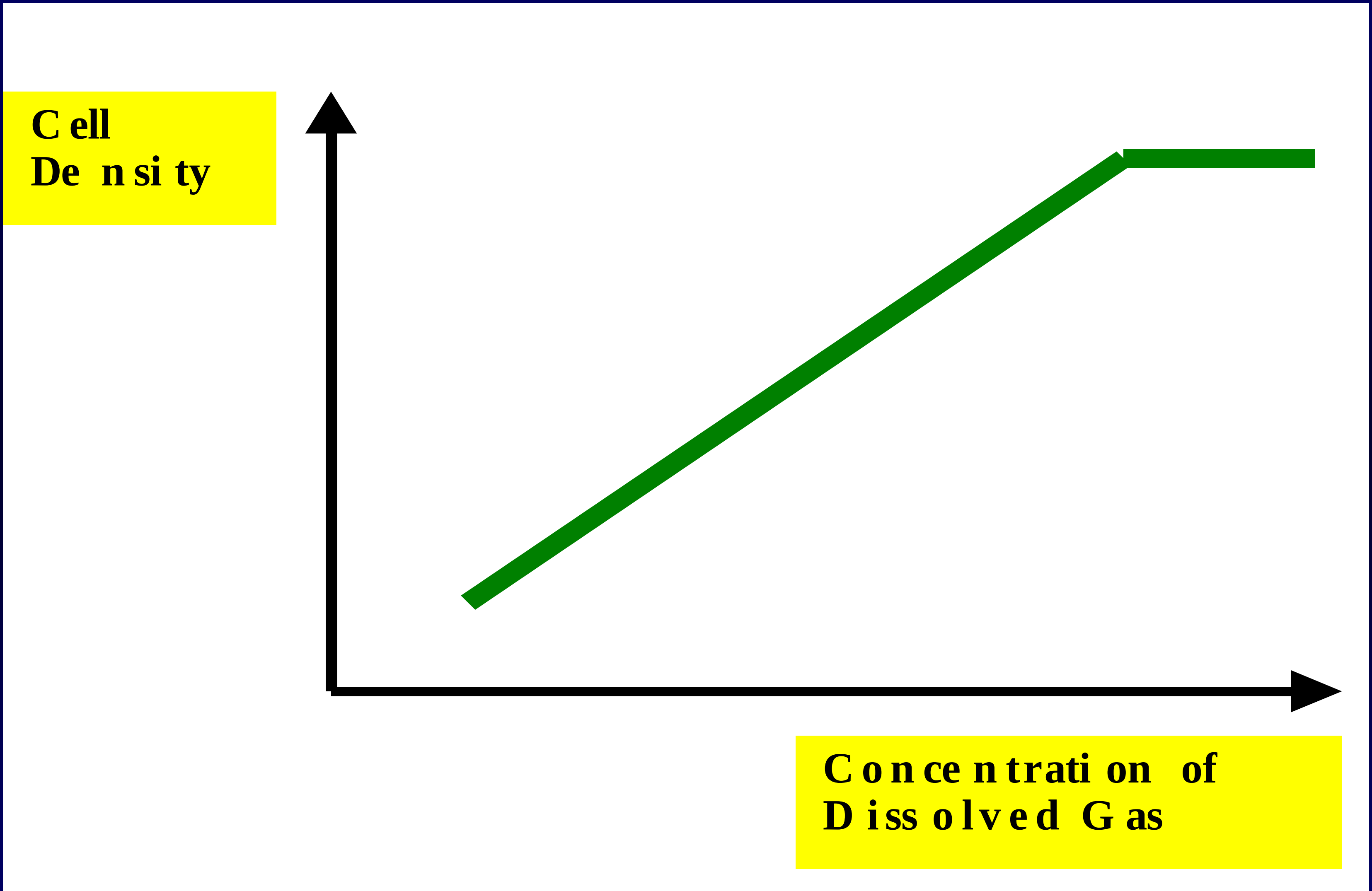
Typical value:

$$\left|\frac{dp}{dt}\right| > 1\ \text{G Pascal / second}$$

How can we make the nucleation cite (N_0) as large as possible?

1. Increase the level of supersaturation!!
2. Don’t put nucleating agent!!
3. Introduce internal strains by stretching, etc.

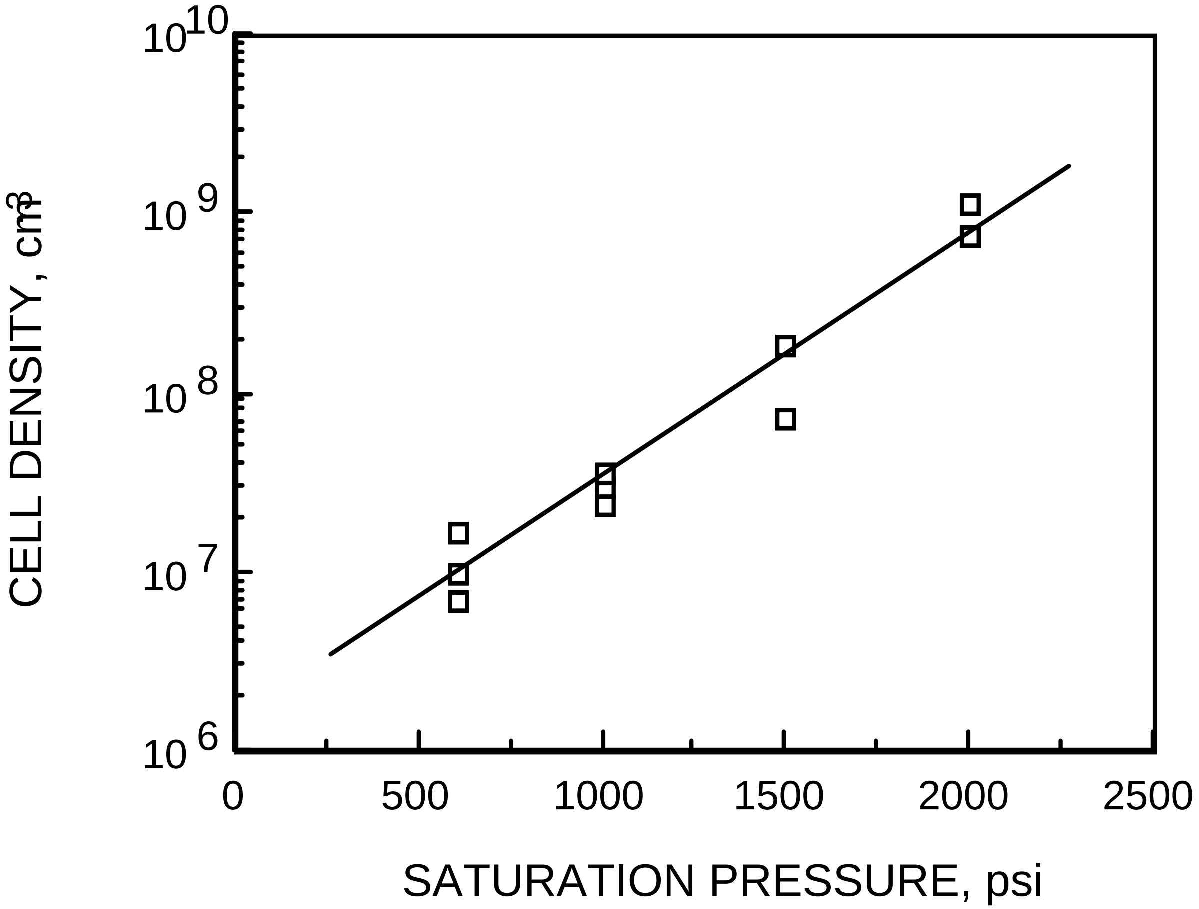
Cell Density vs % Gas Dissolved



CELL NUCLEATION DENSITY

Polystyrene as a function of N_2 Sat Pressure

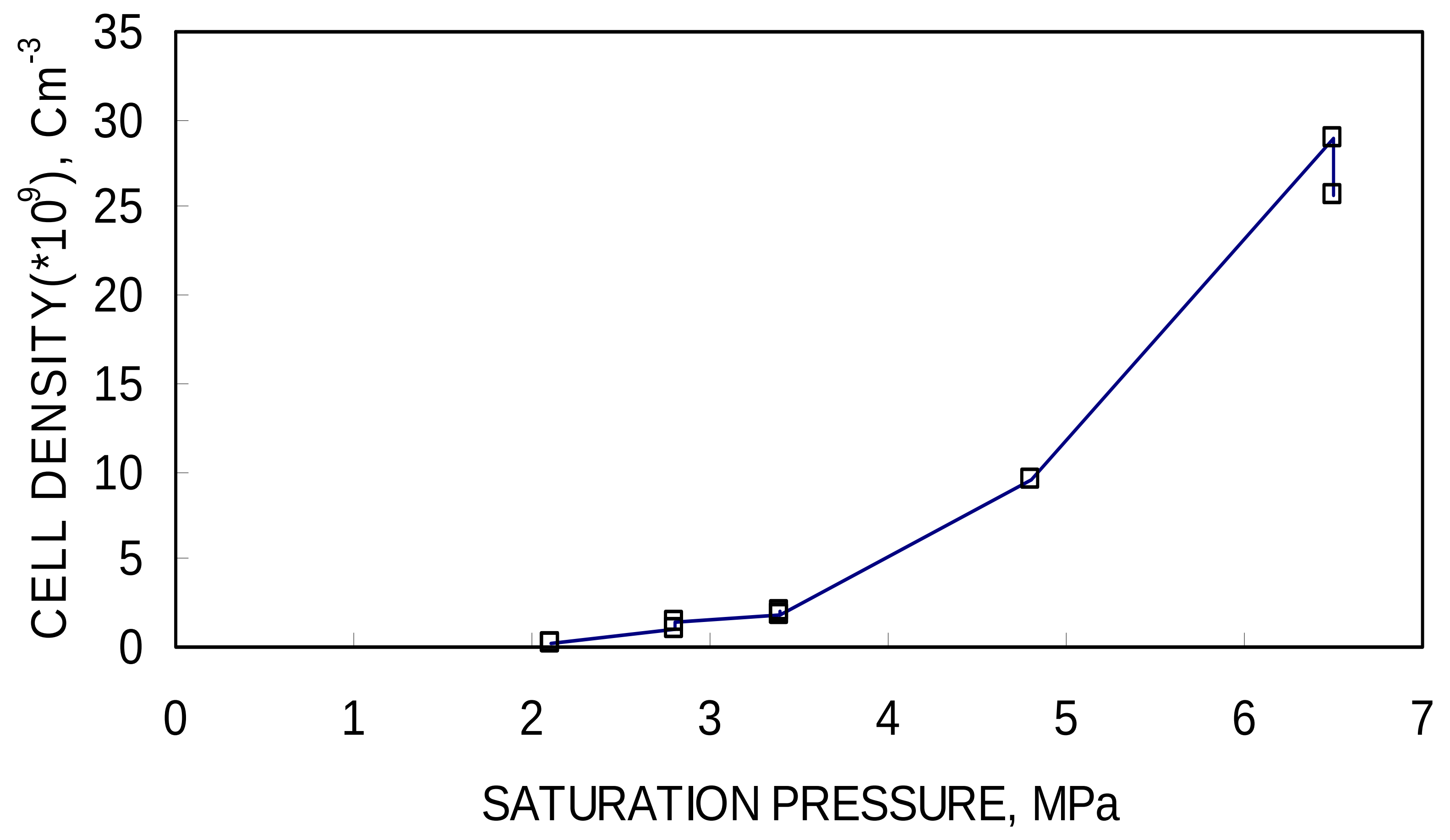
(from Kumar, Ph.D. Thesis, MIT)



CELL NUCLEATION DENSITY

Polycarbonate as a function of N_2 Sat. Pressure

(From V. Kumar, 2000)



Physics of the Continuous Process

3. Cell Growth

Physics of the Process

Cell Growth in a Batch or Continuous Process *(From Baldwin, Ph.D. Thesis, MIT)*

Governing Relationships

$$\rho\left[\frac{3}{2}\left(\frac{dR_{cell}}{dt}\right)^2 + R_{cell}\frac{d^2R_{cell}}{dt^2}\right] = -4\frac{\mu}{R_{cell}}\frac{dR_{cell}}{dt} + \left(P_g - P_\infty - \frac{2\sigma}{R_{cell}}\right)$$

$$\frac{\partial}{\partial t}\left(\frac{P_g R_{cell}^{\;3}}{RT}\right) = 3\rho_p D r^2 \frac{\partial c}{\partial r}\Big|_{R_{cell}}$$

$$\frac{\partial c}{\partial t} + \frac{R_{cell}^{\;2}\dfrac{dR_{cell}}{dt}}{r^2}\frac{\partial c}{\partial r} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D\frac{\partial c}{\partial r}\right)$$

Physics of the Process

Cell Growth in a Batch or Continuous Process

Initial condition

$$c(r, 0) = c_i$$

Boundary conditions

$$c(R_{cell}, t) = K_s P$$

$$\left(\frac{\partial c}{\partial t}\right)_{t, r \to \infty} = 0$$

Physics of the Process

Cell Growth in a Batch or Continuous Process

Cell Size Control in Free Expansion

$$\frac{\textit{Forces due to the pressure in the bubble}}{\textit{Viscous forces resisting the expansion}} = 1$$

$$\frac{f\,(p, T_{gas}, r\,)}{g(\,T_{exterior\ \ layer}\,, \partial T \big/ \partial r_{\ exterior\ \ layer}\,,\ \eta)} = 1$$

Physics of the Process

Cell Growth in a Batch or Continuous Process

Cell Size Control by Imposition of Geometric Constraint

$$\frac{\textit{Free expansion of bubbles}}{\textit{Geometric constraints}} = 1$$

$$\frac{\sum_{n} \Delta v_i}{g(Geomtry)} = 1$$

Physics of the Process

For Uniform Cell Growth in an Intermittent Processes

$$\frac{\text{Characteristic flow rate in the mold}}{\text{Rate of expansion of cells}} > 1$$

$$\frac{f(V_{injection})}{g(\eta, T_{polymer}, c_{total\ gas}, \alpha_{gas\ in\ polymer})} > 1$$

Design of a Continuous Process

- FRs --> DPs

- DPs --> PVs

Design of a Continuous Process for Sheet Extrusion

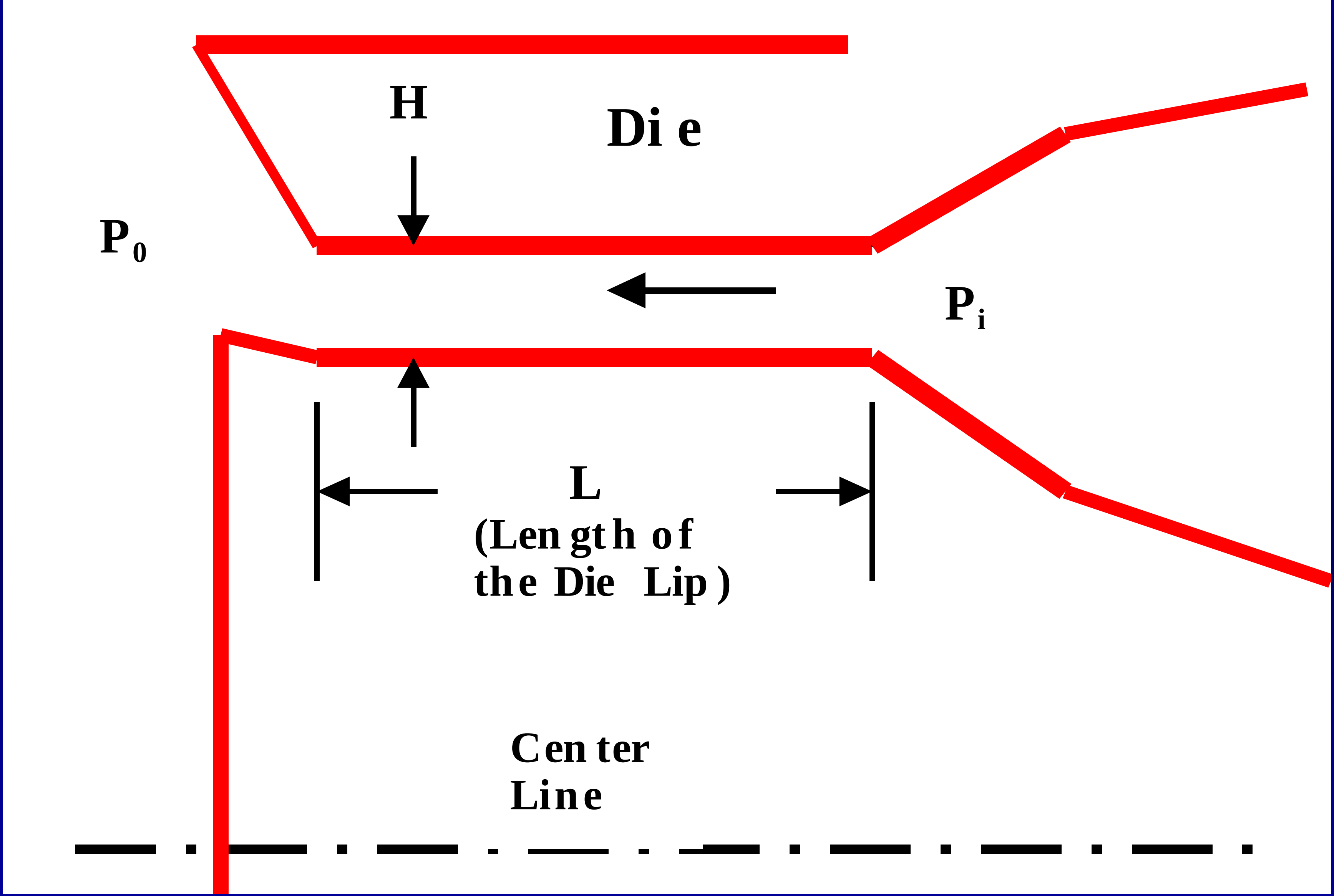
The highest level FRs

FR1 = Control cell size

FR2 = Control the number of cells

FR3 = Control the geometry of the extrudate

Design of a Tube Die



Design of Microcellular Plastics Process

The corresponding design parameters (DPs) are:

DP1 = P_i*

DP2 = dp/dt

DP3 = Die shape & Accessories

* Assuming that P_i* is the saturation pressure for the dissolved gas.

Design of Microcellular Plastics

The design equation may be written as

$$\begin{Bmatrix} \text{Cell size} \\ \text{Cell density} \\ \text{Geometry} \end{Bmatrix} = \begin{bmatrix} X & x & 0 \\ X & X & 0 \\ x & 0 & X \end{bmatrix} \begin{Bmatrix} P_i \\ dp/dt \\ Die\,\&\,Acc. \end{Bmatrix}$$

Design of Microcellular Plastics Process

FR3 and DP3 must be decomposed to develop detailed means of controlling the geometry.

Design of Microcellular Plastics

The corresponding Process Variables (PVs) are:

PV1 = Extruder rpm, Ω

PV2 = Die length, L

PV3 = Means of controlling the geometry of the extrudate

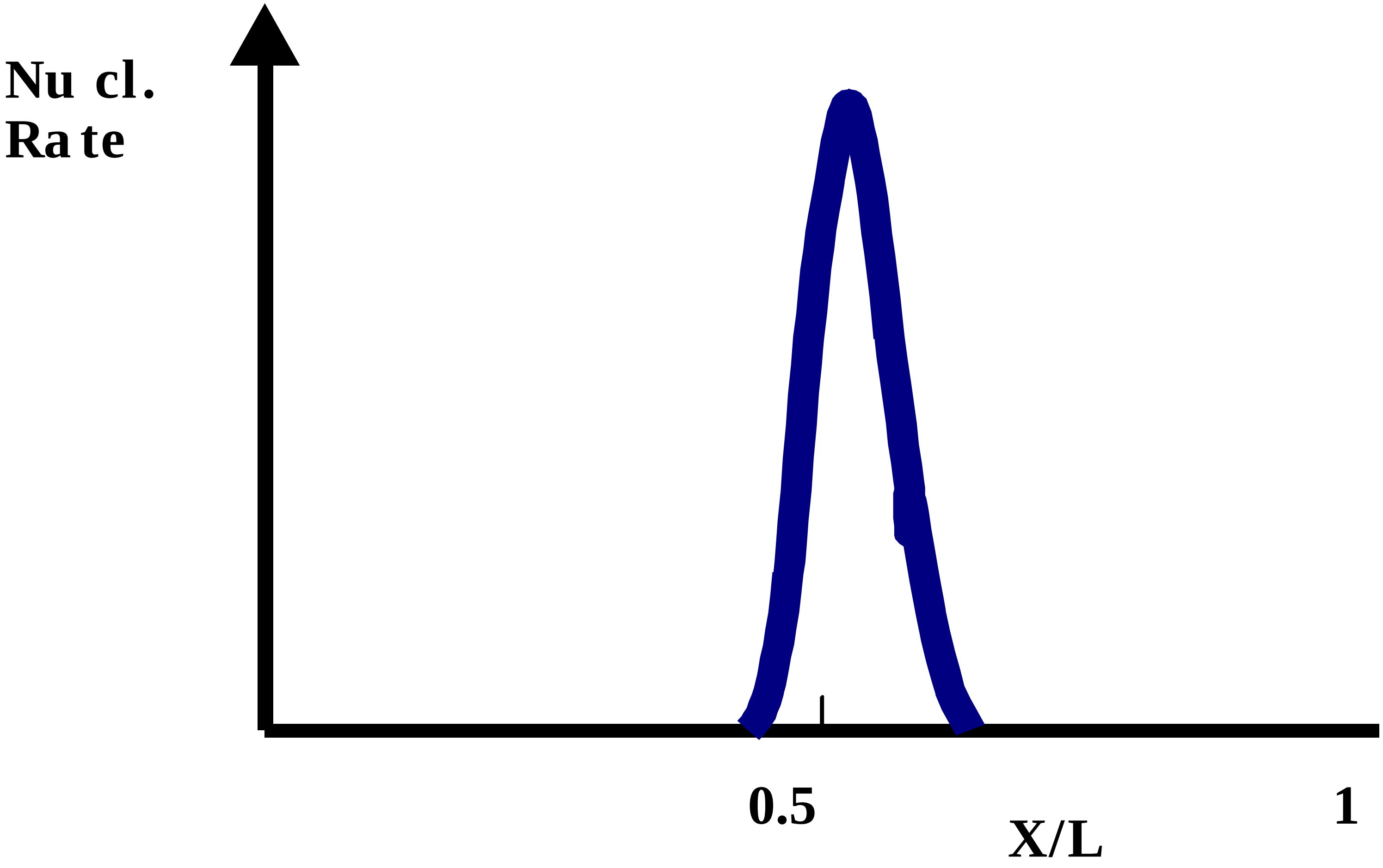
Design of Microcellular Plastics

The corresponding design equation for the process :

$$\begin{Bmatrix} P_i \\ dp/dt \\ Die\ \&\ Acc. \end{Bmatrix} = \begin{bmatrix} X & x & 0 \\ X & X & 0 \\ 0 & 0 & X \end{bmatrix} \begin{Bmatrix} \Omega \\ L \\ Means\ldots \end{Bmatrix}$$

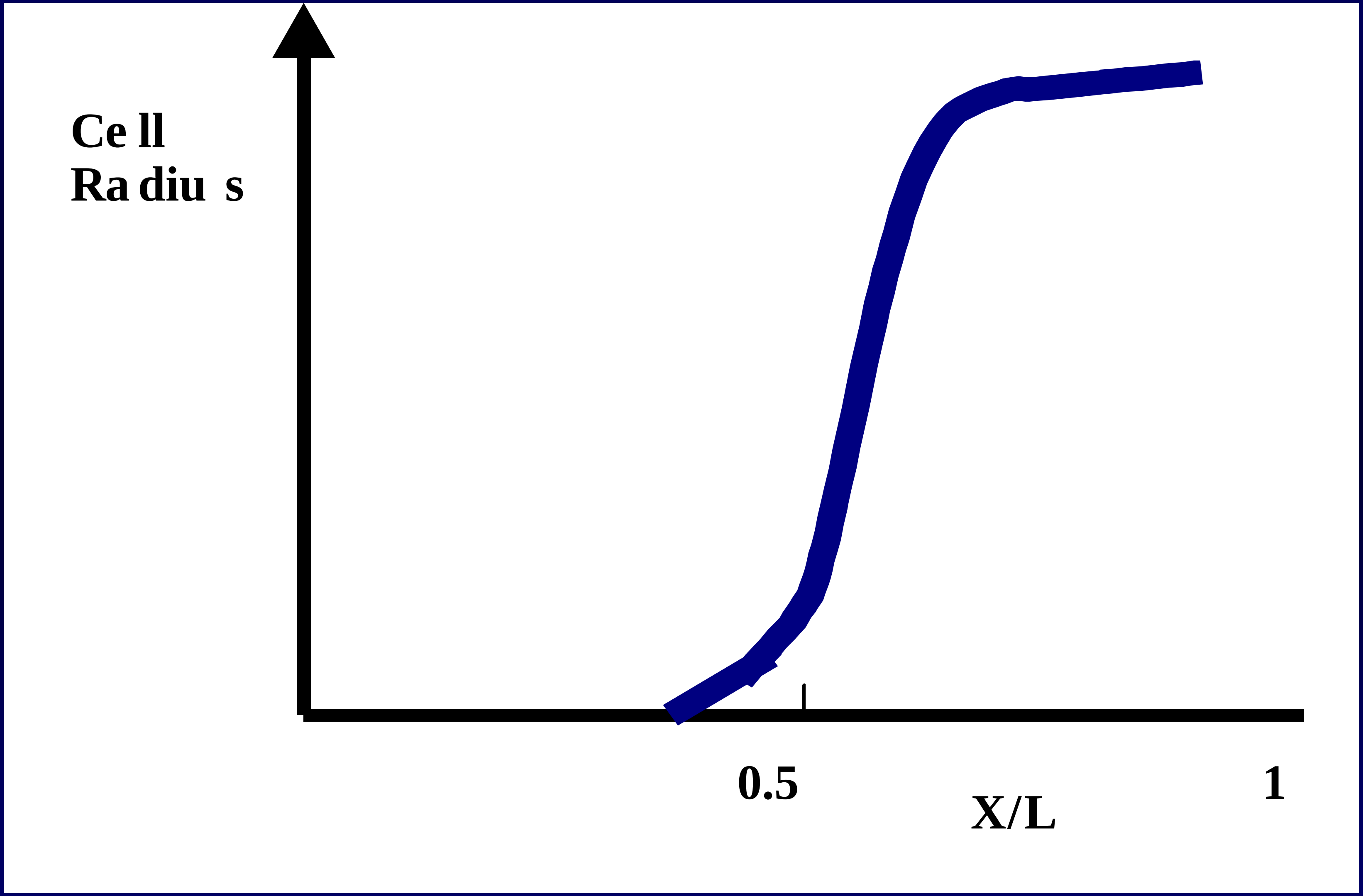
Typical Nucleation Rate in a Parallel Die

Schematic Diagram Adapted from Sanyal, PhD. Thesis, MIT



Typical Cell Growth in a Parallel Die

Schematic Diagram Adapted from Sanyal, PhD. Thesis, MIT



Design of a continuous Process

Graph removed for copyright reasons.

Representative pressure profile along the polymer flow field in the extruder and die (From Baldwin, Park and Suh, 1997)

Design of a continuous Process

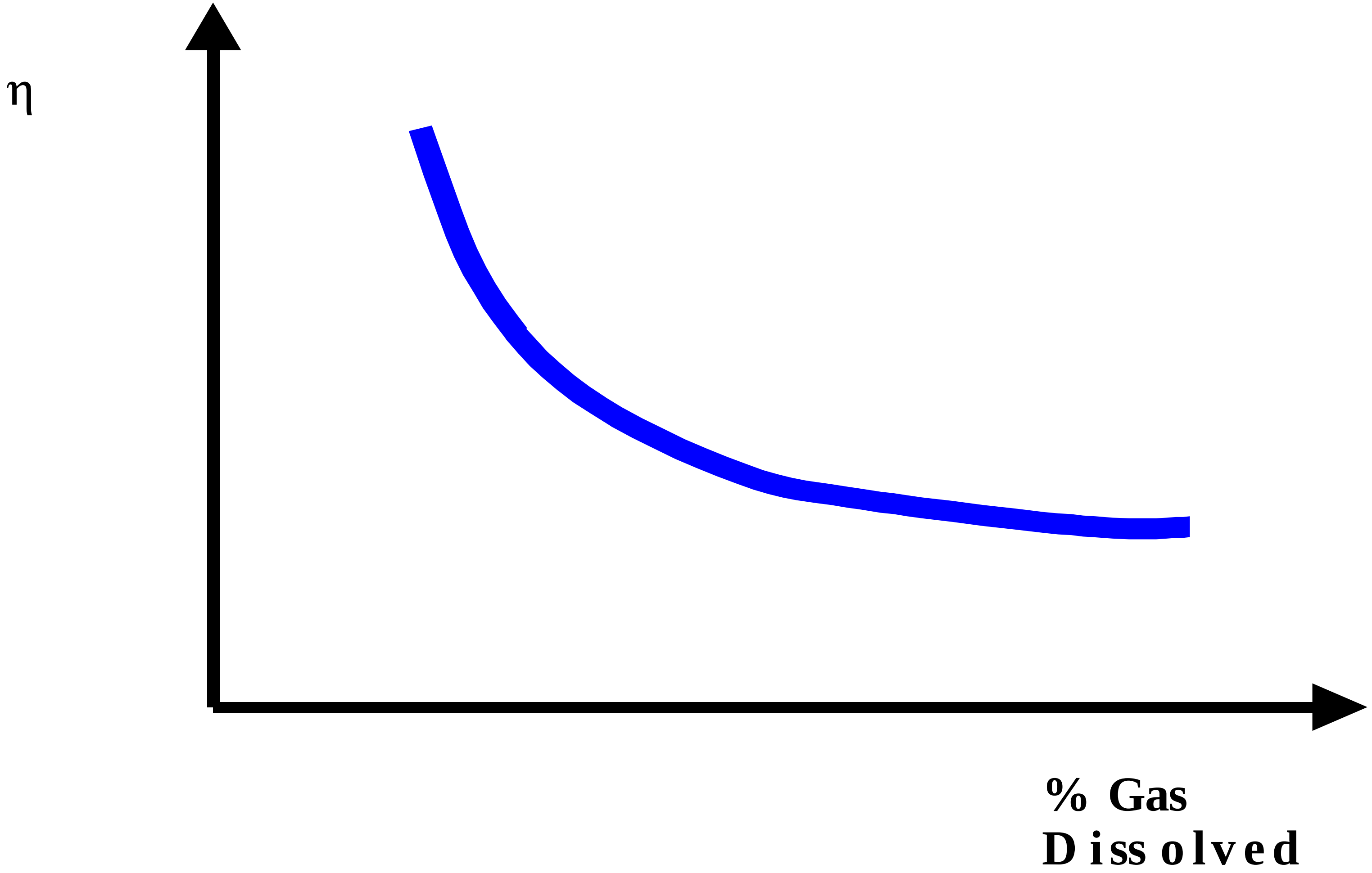
Diagram removed for copyright reasons.

Figure 7.16 Schematic of the Microcellular extrusion system used for the shaping and cell growth control experiments (From Baldwin, Park and Suh, 1997)

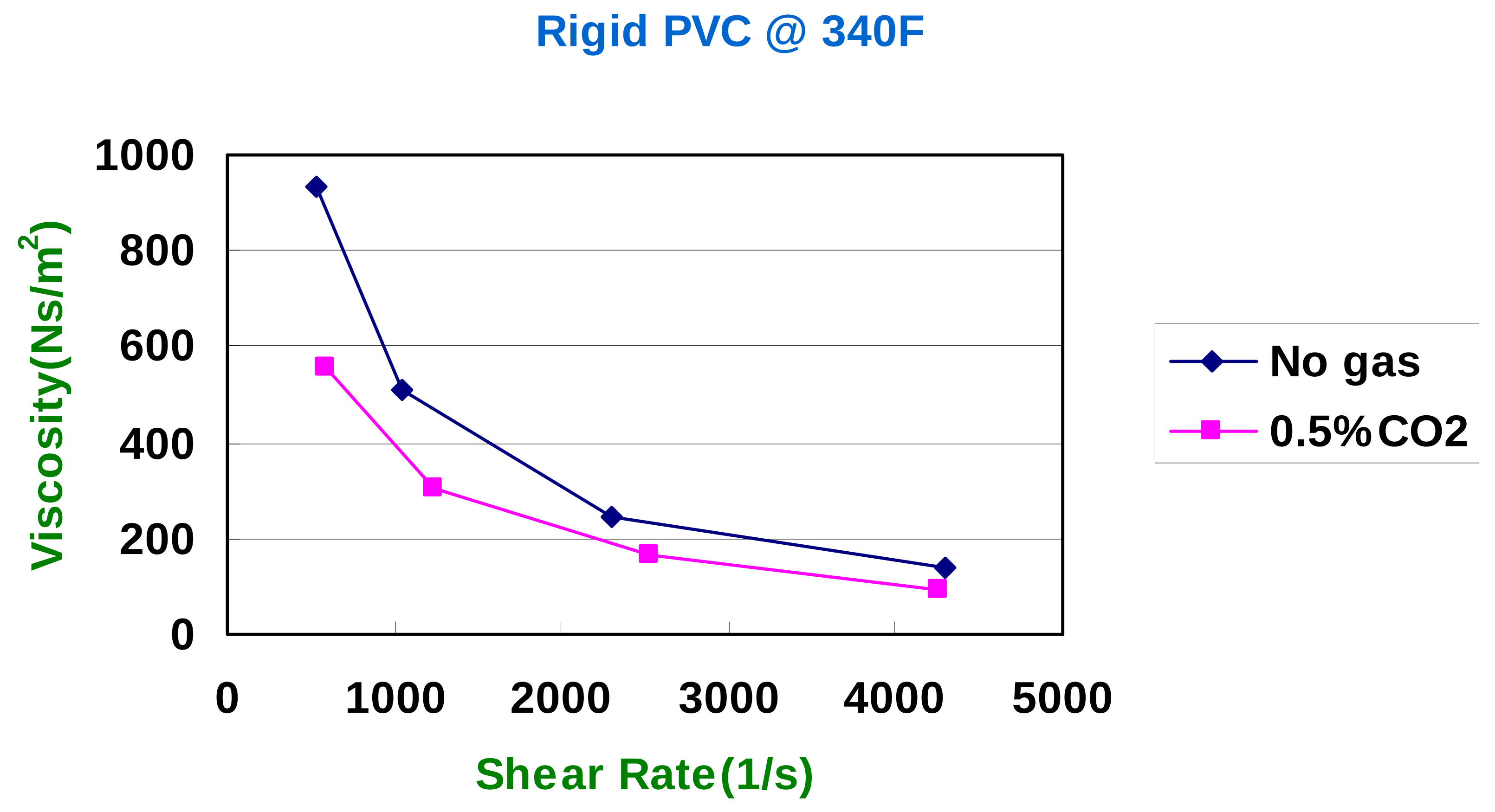
Unanticipated Processing Advantages of Microcellular Plastics

- *Decrease in viscosity*
- *Lowering of the melting point and glass transition temperature*
- *Elimination of shrinkage*

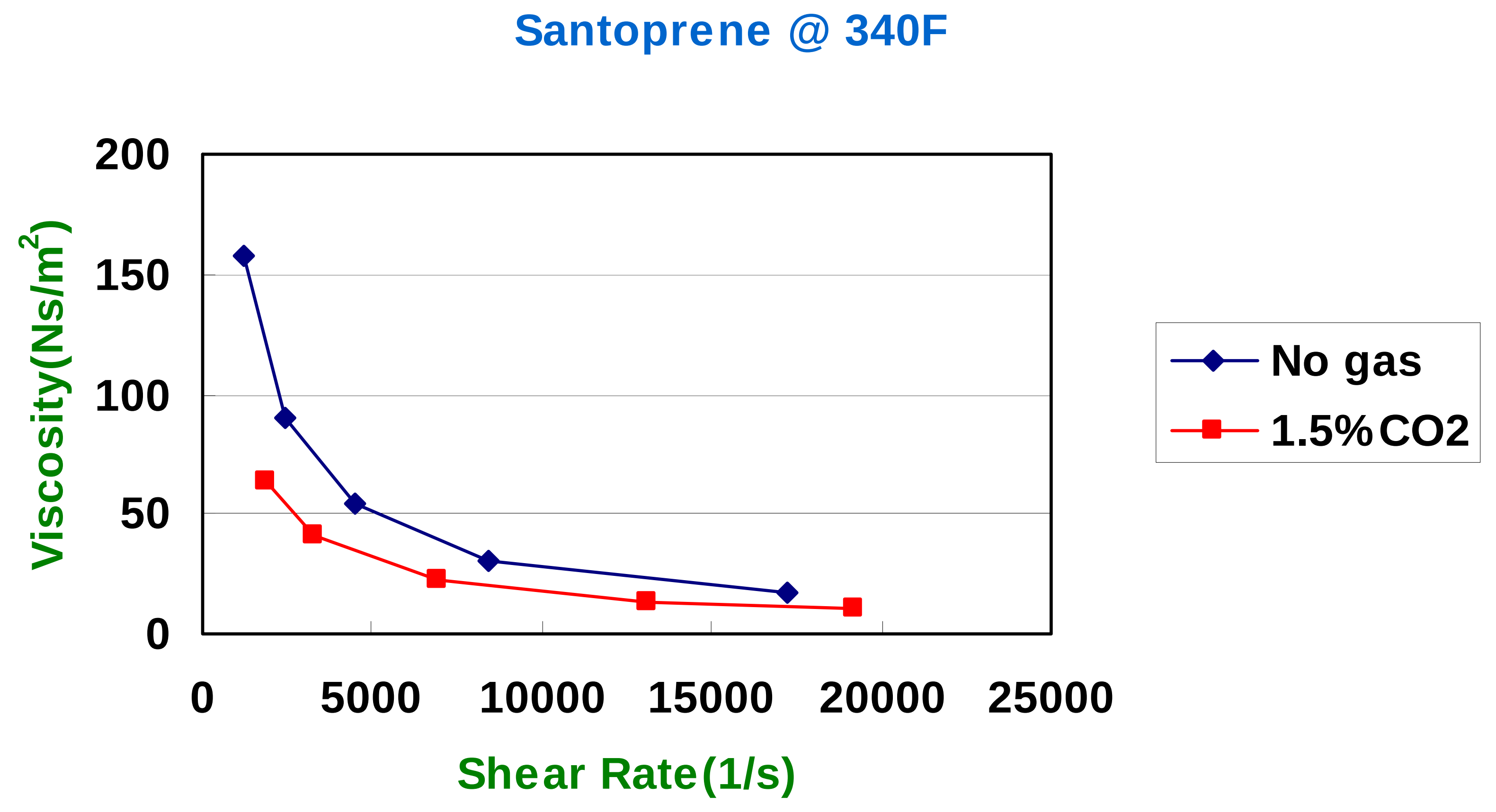
Effect of CO_2 on Physical Properties: Viscosity



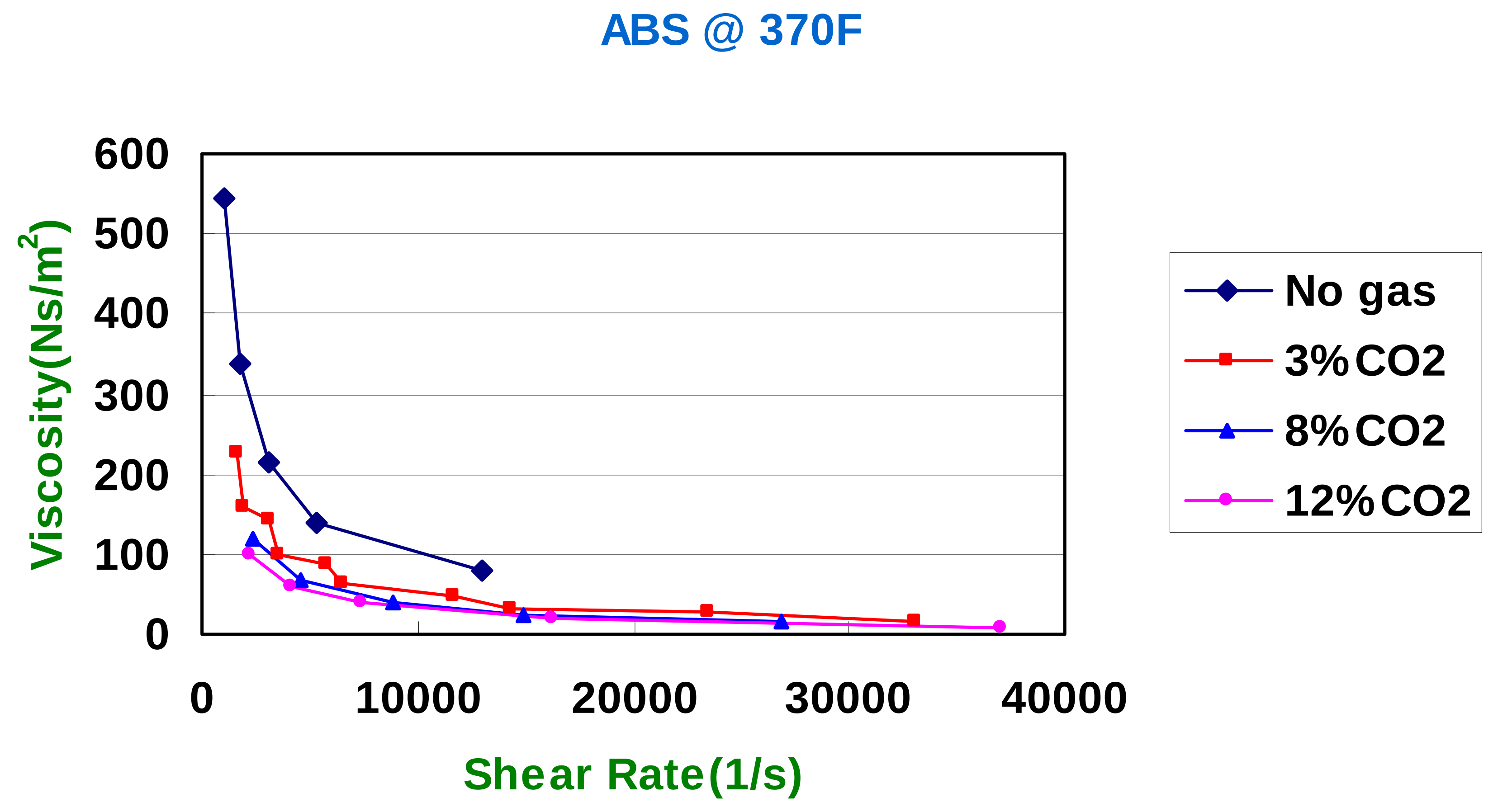
Rigid PVC @ 340F



Santoprene @ 340F



ABS @ 370F


ABS @ 370F
600
500
400
300
200
100
0
Viscosity(Ns/m2)
0
10000
20000
30000
40000
Shear Rate(1/s)
No gas
3% CO2
8% CO2
12% CO2

Glass Transition Temperature

DMA result (PETG) [From Cha & Yoon, 2001]

Graph removed for copyright reasons.

Behavior of PETG material as a function of temperature.
Elastic modulus sharply decreases around the **glass transition temperature**

Models for estimating Tg [From Cha & Yoon, 2001]

Chow’s Model (1980)

$$\ln\left(\frac{T_g}{T_{go}}\right) = \beta\left\{(1-\theta)\ln(1-\theta)+\theta\ln\theta\right\}$$

Cha-Yoon Model (1998)

$$T_g = T_{go}\exp\left[-(M_p)^{-1/3}(\rho)^{-1/4}\alpha\omega\right]$$

ρ : specific density of polymer

α : material constant

ω : % solubility for carbon dioxide in polymer (weight gain)

Glass Transition Temperature

[From Cha & Yoon, 2001]

- Comparison of the Two Models

Two graphs removed for copyright reasons.

Experimental results of T_g of PETG

Comparison of Cha-Yoon model vs. Chow's model

Microcellular Foaming/Forming

- **Thermoforming : the process of manufacturing products from a thermoplastic sheet heated to its softening point and formed by pressure difference into a molded shape**

Figure removed for copyright reasons.

Experimental

- ▪- Cha-Yoon model indicates when the weight fraction of CO2 dissolved in PETG is 7.7% the T_g is lowered to room temperature

Photographs of two cups made through microcellular foaming/forming experiment at room temperature

Photo removed for copyright reasons.

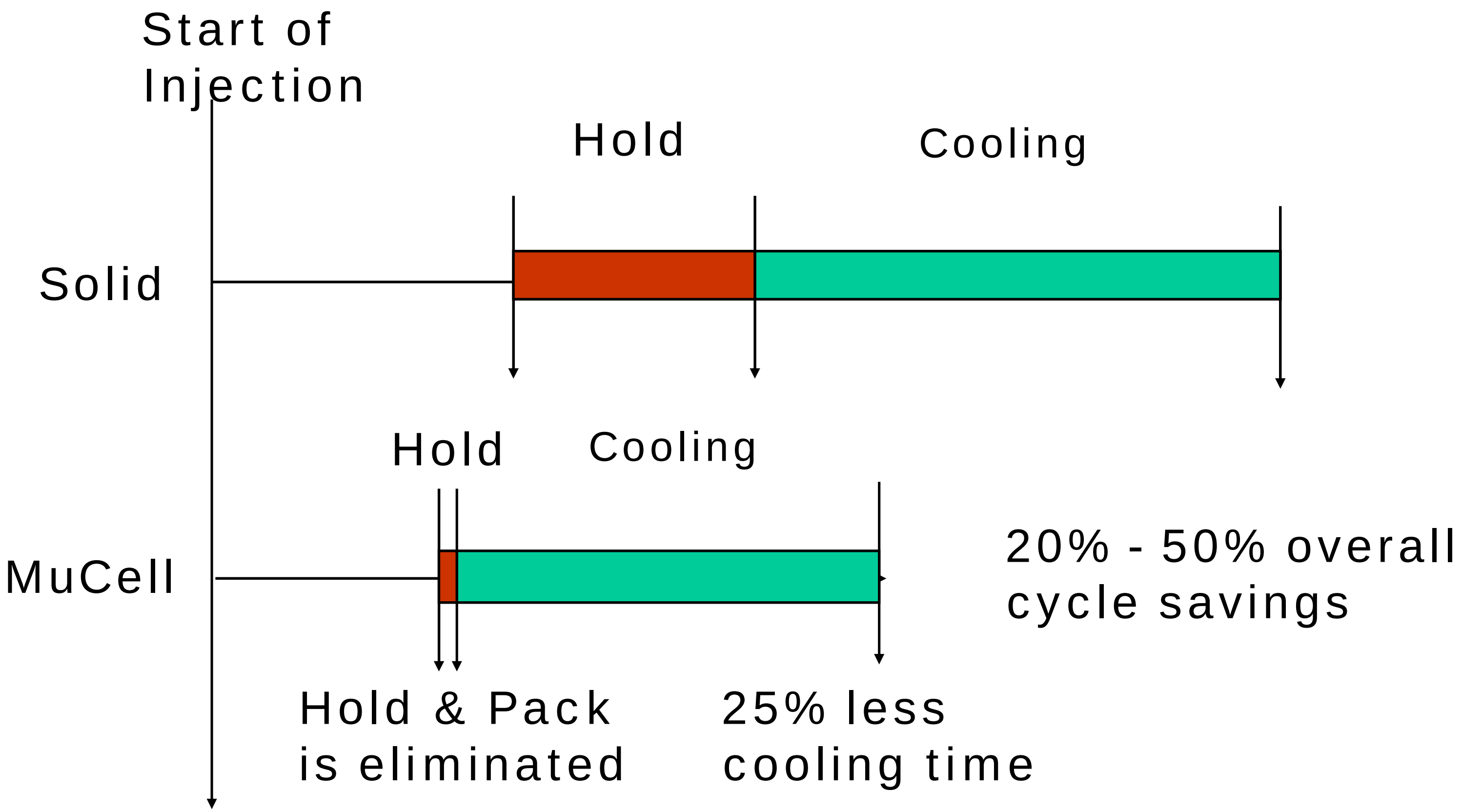
Effect of Dissolved Gas on Processing of Microcellular Plastics

- ***Higher throughput rate by as much as 50%***

- ***Faster cycle time by as much as x2***

- ***Precision parts***

Cycle Time Reduction



Start of Injection

Hold

Cooling

Solid

Hold

Cooling

MuCell

Hold & Pack is eliminated

25% less cooling time

20% - 50% overall cycle savings

MuCell™ Molding Technology

Office Equipment

Dimensional Stability Required:

- Glass filled engineering resins such as PPO, PC or PC/ABS
- Out of spec product made to spec. using MuCell Molding Technology
- 50% reduction in warpage - .060 to .027
- 25% reduction in cycle time, 8% weight reduction

Photo removed for copyright reasons.

Printer Chassis

MuCell™ Molding Technology

Impact Performance

Printer Chassis:

- 35% Glass/Mineral filled PPO/HIPS
- 8% weight reduction

Photo removed for copyright reasons.

	Drop Weight Impact	Notched Izod Impact
Solid	6.7 ft-lb	7.3 kJ/m^2
8% Wt. Red.	9.0 ft-lb	9.7 kJ/m^2