97th AOCS Annual Meeting
FS & FF 2: Role of Polymers in Foods
St. Louis, MO    May 1, 2006

# THE "FOOD POLYMER SCIENCE" APPROACH TO FOOD STRUCTURE AND FUNCTIONALITY

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# FAR FROM EQUILIBRIUM

## PRACTICAL PROBLEMS OF FOOD SCIENCE AND TECHNOLOGY

- GRAININESS AND ICINESS IN ICE CREAM
- CRYOPROTECTION AND CRYOSTABILIZATION OF FROZEN OR FREEZER-STORED PRODUCTS
- BAROPROTECTION
- SUGAR AND FAT BLOOM
- CAKING AND STICKINESS OF DRY POWDERS
- COOKING OF CEREALS AND GRAINS
- EXPANSION, COLLAPSE, AND STALING OF BAKED GOODS
- RAW MATERIAL SELECTION AND DESIGN
- GELATIN MANUFACTURING AND CONSUMER CONVENIENCE

# BEYOND WATER ACTIVITY

MOISTURE MANAGEMENT

WATER DYNAMICS

← WHAT IS THE LINK ? →

PROCESS CONTROL
STORAGE STABILITY

GLASS DYNAMICS

# FOOD POLYMER SCIENCE

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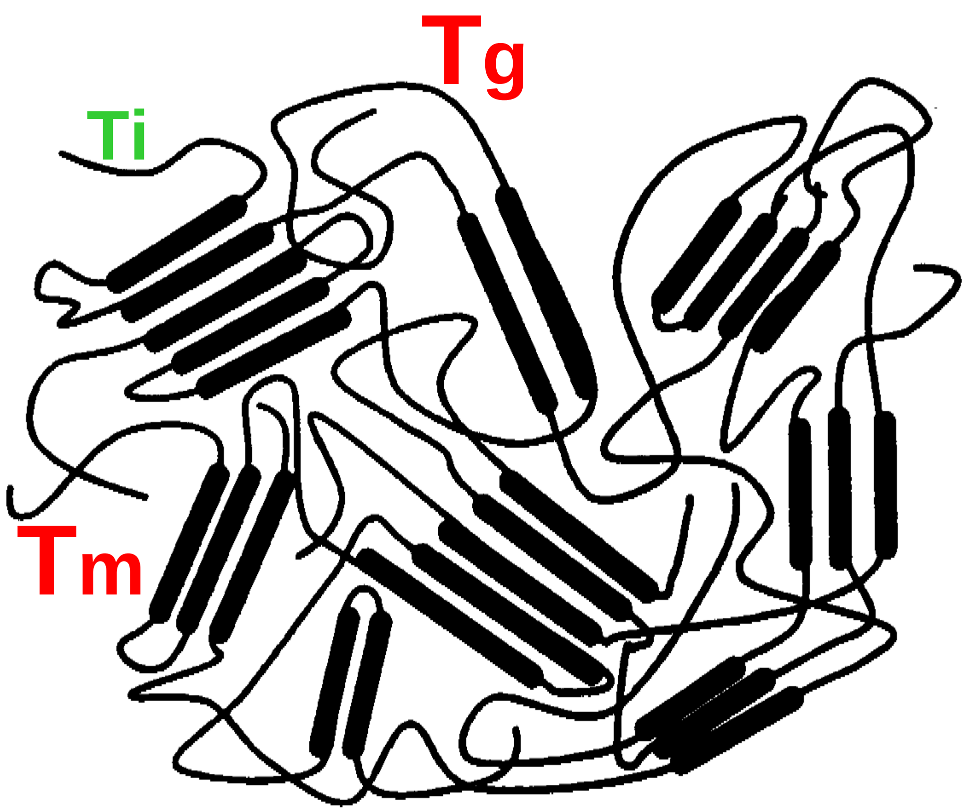
# FOOD POLYMER SCIENCE

## CENTRAL CONCEPT OF FPS APPROACH

### STRUCTURAL ASPECT




10 nm domains

### FUNCTIONAL ASPECT

**DEFINITION OF THE GLASS TRANSITION**

**TEMPORAL** ps to min

**OPERATIONAL**

**mechanical relaxation**

mobility transformations

**time / temperature / pressure / stuctural composition / dimensions**

**DIMENSIONAL**

**BIG polymers ↔ SMALL plasticizers**

**diffusion distances**

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# FOOD POLYMER SCIENCE

## STRUCTURAL ASPECT

**Partially crystalline glassy polymers**

**⇒ Non-equilibrium solid state**

**Fringed Micelle Model**

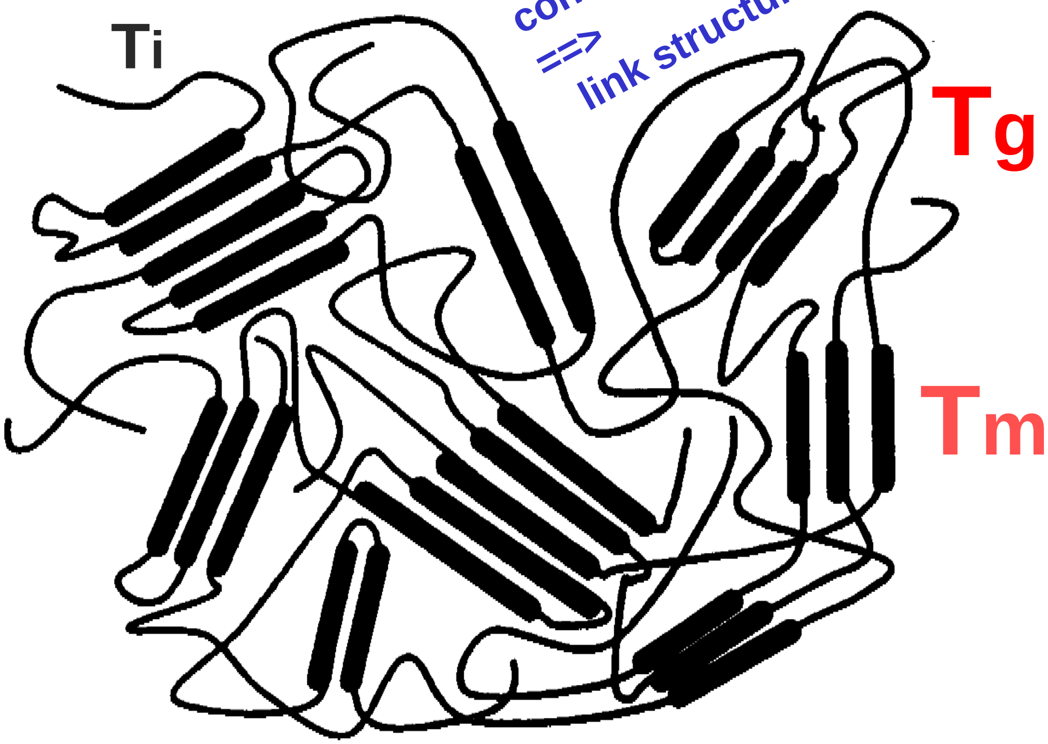
**Homologous families**

**Tg and linear DP predict function**

**Nonhomologous families**

**Tm/Tg predicts function**

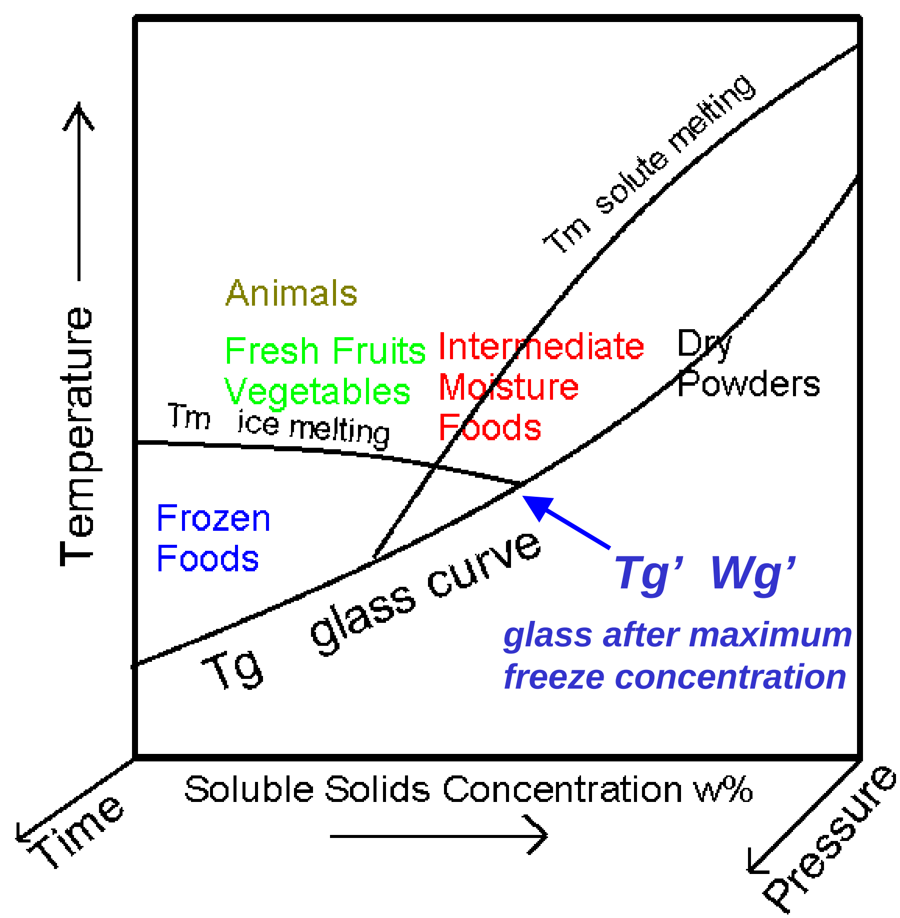
**Tg and Tm define temperature domains**
**control relaxation timescales**
**==> link structure to function**




## FUNCTIONAL ASPECT

**Mobility transformations**

**Snapshot for ~10nm diffusion distances**

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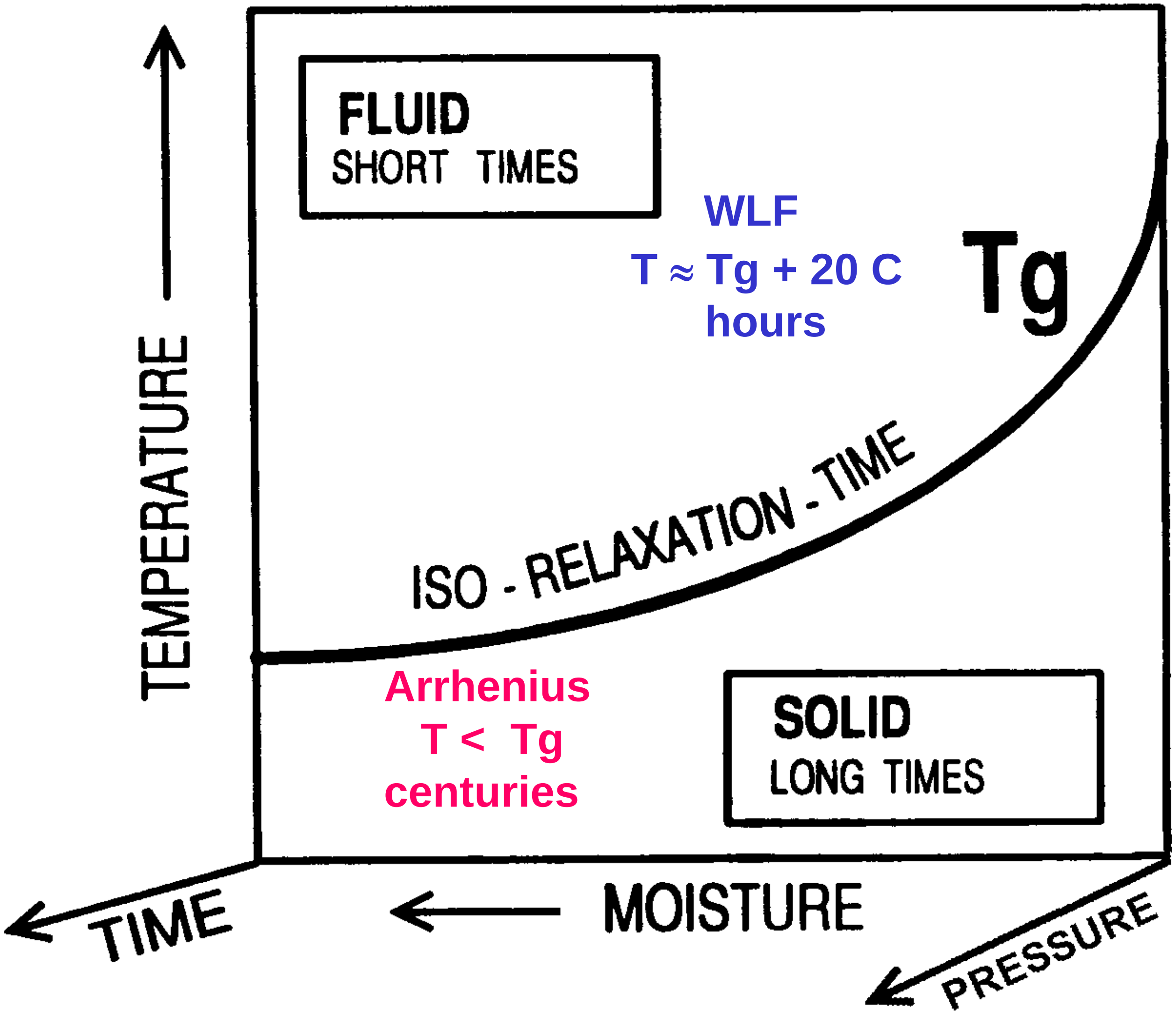
# TEMPORAL DEFINITION OF Tg

**MOBILITY TRANSFORMATIONS**

Tg CURVE OF ISO-RELAXATION-TIME
AS MATERIAL-SPECIFIC REFERENCE CONTOUR TO RELATE
TIME - TEMPERATURE - PRESSURE - DIMENSIONS -
MOISTURE CONTENT - SOLUTE TYPE

Arrhenius
T > Tm
nanosec




Tg and Tm define Tdomains
control relaxation timescales
=> link structure to function

Tg + 10° 36 days
If process at Tg = century
Tg - 10° 200 years

Dramatic evolution of
timescales in “parallel”
contours above Tg
WLF kinetics

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# OPERATIONAL DEFINITION OF $T_g$

## ORIGIN OF FUNCTIONAL DOMAINS OF TEMPERATURE

## WLF KINETICS

### PHYSICO-CHEMICAL MECHANISM OF RELAXATION PROCESSES

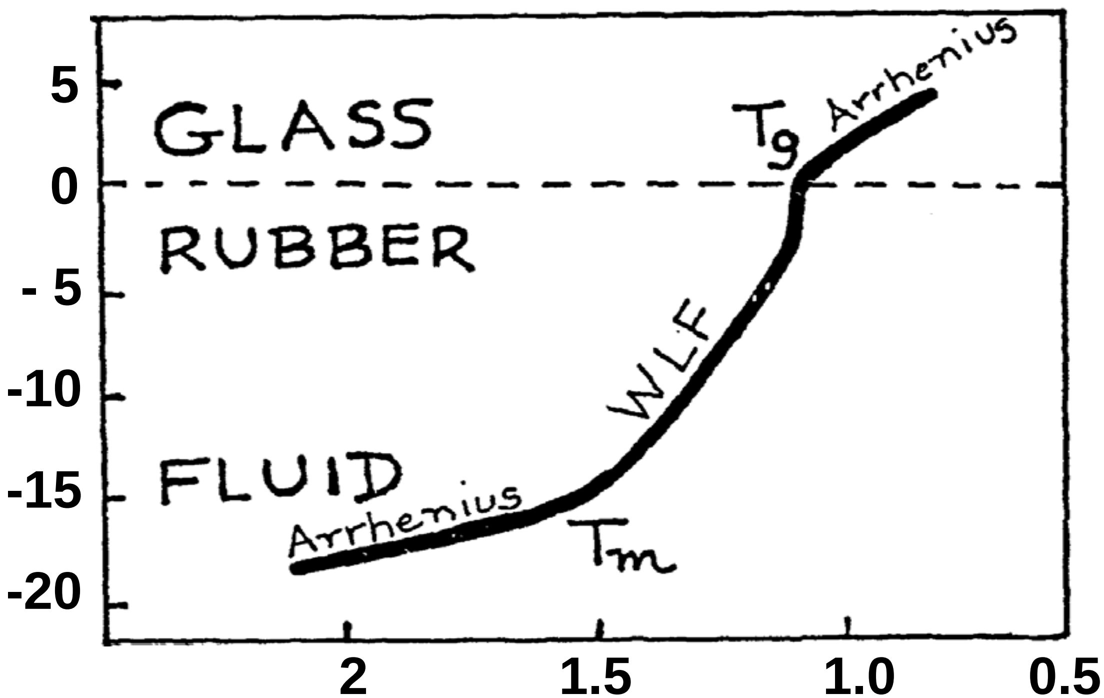
$$\log \eta/\eta_g = \frac{-A\,(T - T_g)}{B + (T - T_g)}$$

$\log \eta/\eta_g$

(poise)

due to

$\log \tau/\tau_g$




T / Tg ( K )

**17 orders of magnitude from Tm to Tg !!**

*S. aureus* 0.5 μ
trip across wheat
starch granule 30 μ
takes a century
in the glassy state

SAME COEFFICIENTS IN WLF EQUATION FOR TYPICAL SYNTHETIC POLYMERS, ANHYDROUS GLUCOSE, AND SUCROSE SOLUTIONS BUT NOT FRUCTOSE

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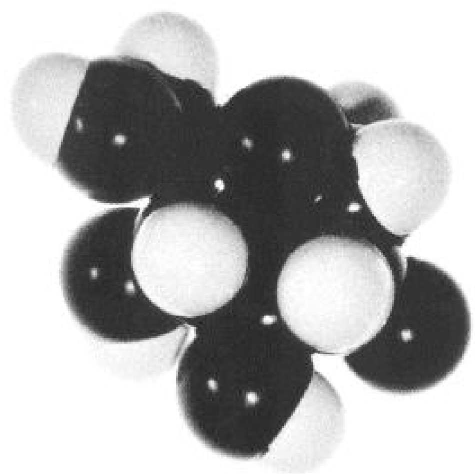
# DIMENSIONAL DEFINITION OF $T_g$



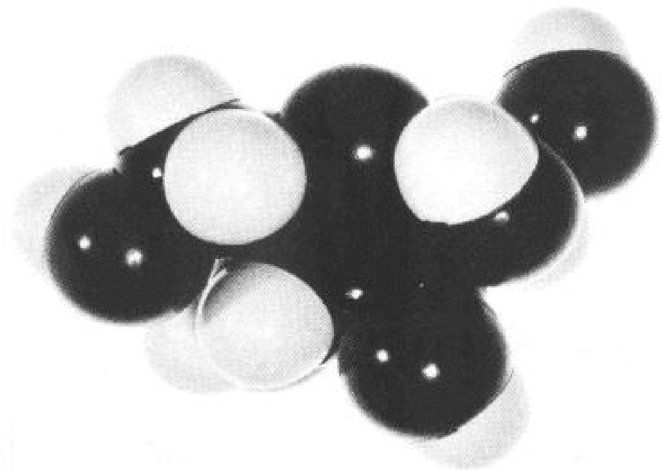
α-D-Glucopyranose

TRANSLATIONAL CONSTRAINT

Tm / Tg ~ 1.42

Tg 31°C

Tg' - 43°C



β-D-Fructofuranose

ROTATIONAL CONSTRAINT

Tm / Tg ~ 1.06

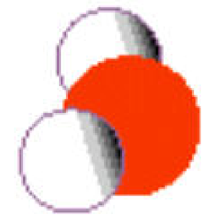
Tg 100°C

Tg' - 42°C

TRANSLATIONAL CONSTRAINT

Tm/Tg ~ 1.39

Tg 12°C



TINY !

$CO_2$

~ 0.512 nm

Water

~ 0.4 nm

TRANSLATIONAL CONSTRAINT

Tm/Tg ~ 2

Tg - 135°C

Nucleation | Growth | Crystallization

Dielectric loss | Microwave heating

Mixture Behavior
1:1 Glucose:Fructose Tg 20°C
Mobility more like glucose alone than like fructose alone

Observed rvp of sample
Microbiological stability
Bulk moisture migration
Baking functionality

6 glucose units = 1 turn amylose helix = 0.8 nm Tg' -14.5°C
18 glucose units ~ 6 DE maltodextrin ~ 2 nm Tg' - 6°C
Biopolymer (globular protein) hemoglobin = 6.4 nm Tg' - 5°C

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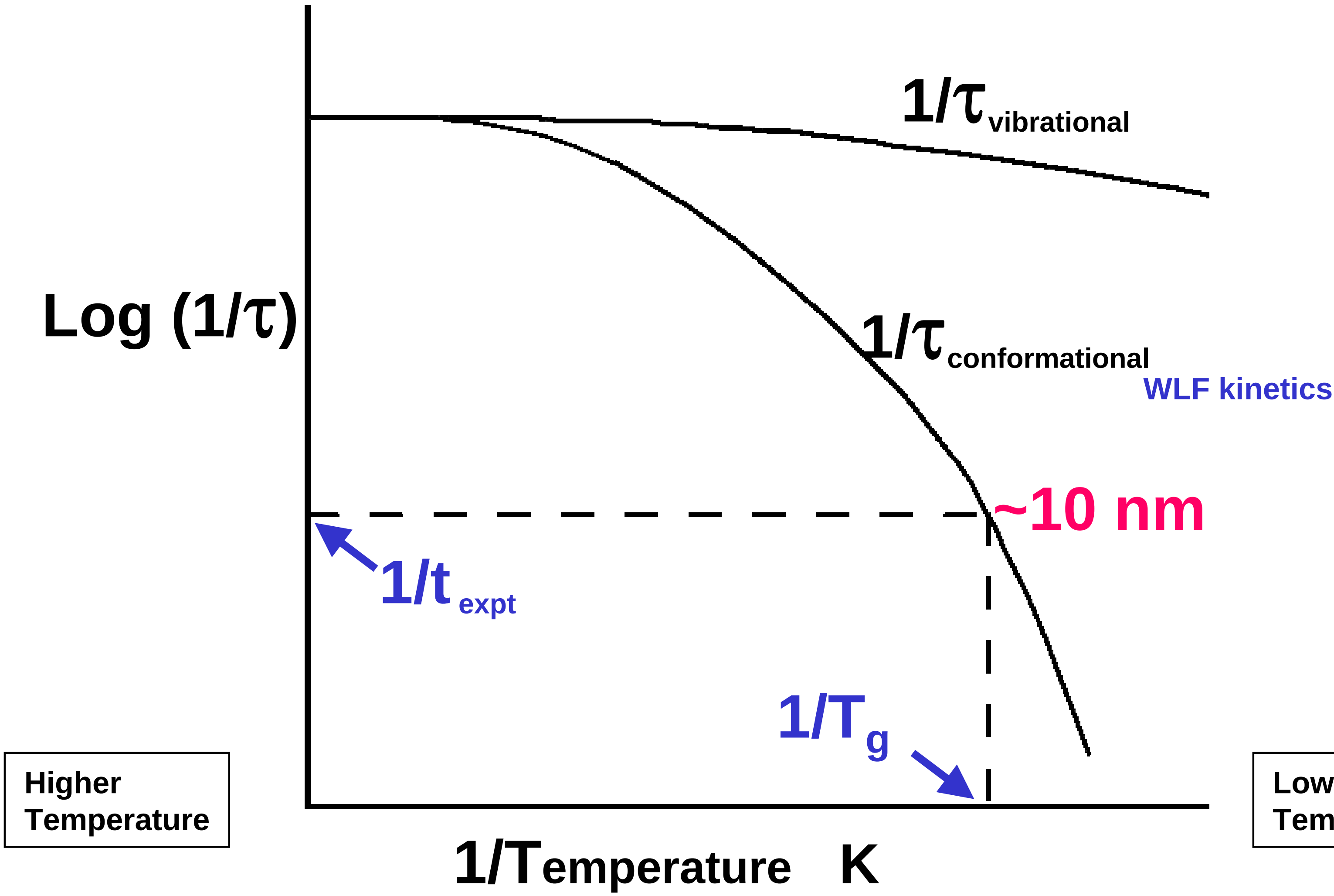
# MOBILITY TRANSFORMATIONS BASED ON TEMPORAL, OPERATIONAL, & DIMENSIONAL DEFINITIONS

**$T_g$ is the temperature at which the allowed experimental time matches the conformational relaxation time in a 10 nm diffusion space**

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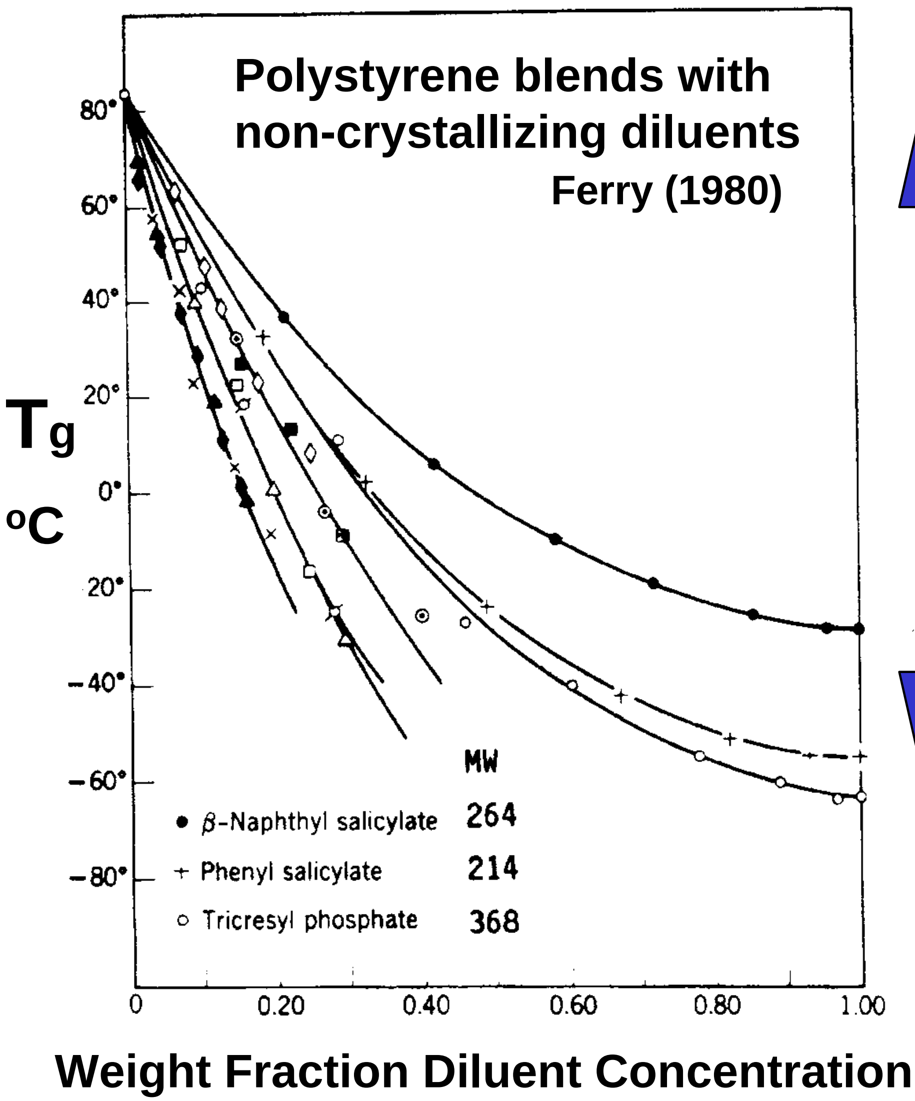
# WHAT IS A PLASTICIZER ?

## A plasticizer depresses initial Tg to below T or increases t / τ




**THE BEST PLASTICIZER**

**is a compatible diluent**

**with the lowest Tg**

**(but not always the lowest molecular weight)**

**Maximum potential plasticization =**

$$Tg_{\text{pure polymer}} - Tg_{\text{pure diluent}}$$

**Plasticization of food polymers by water is potentially excellent (avoid ice)**

**Tg pure diluent ~ -135°C**

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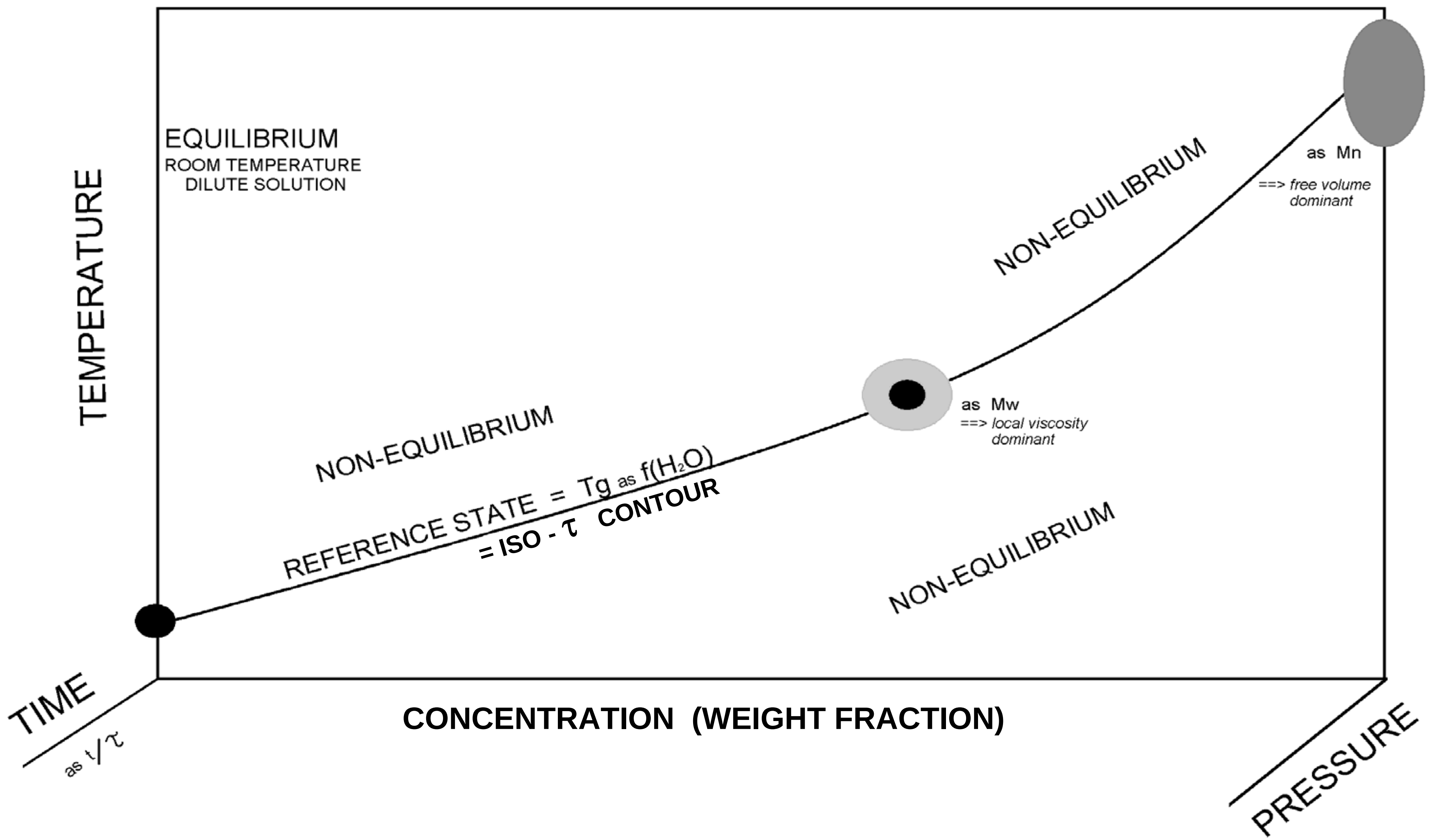
# DEFINITION OF Tg OF A BLEND

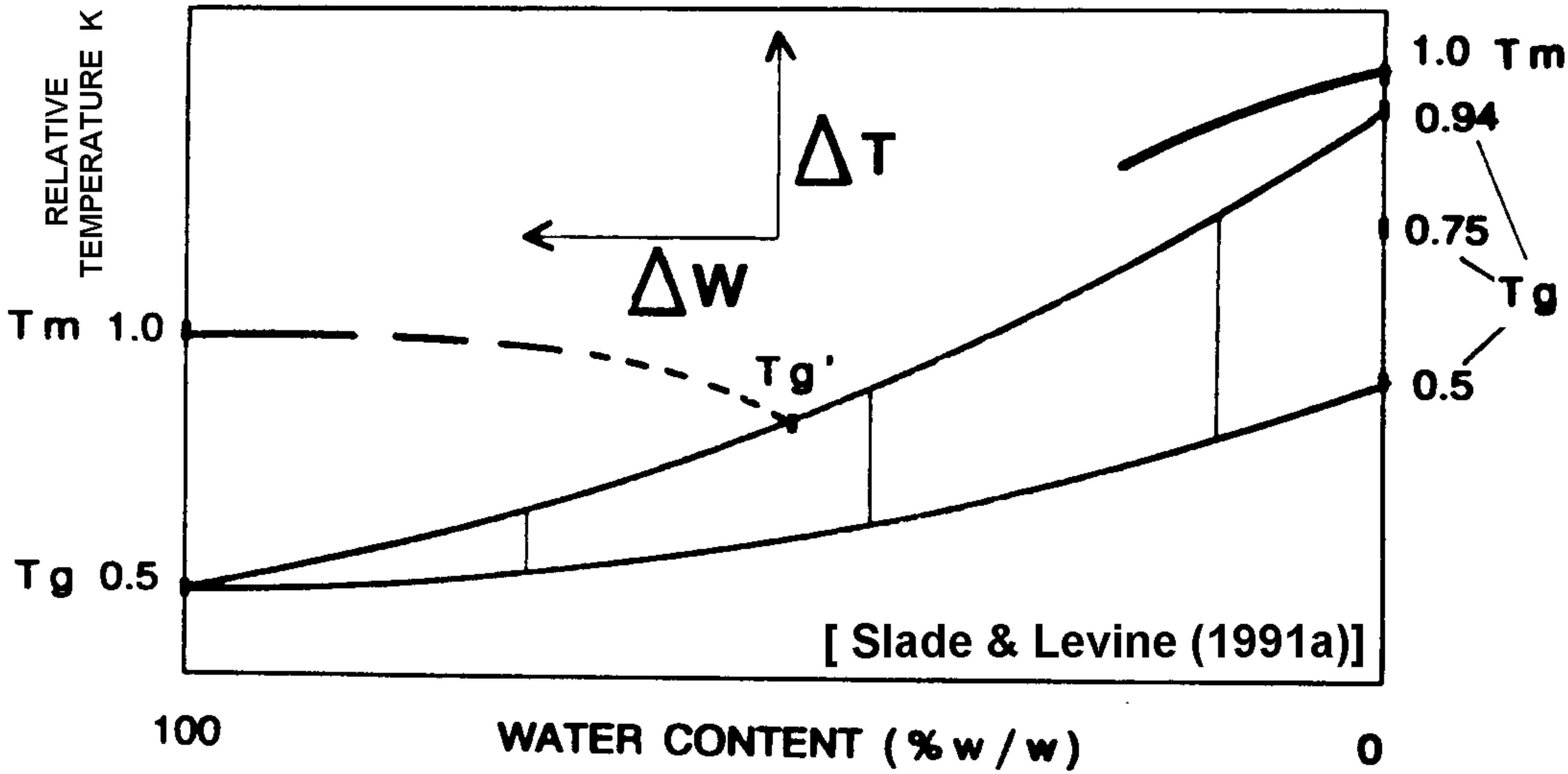
**Tg of a blend = Tg of "reporter molecule" with $\tau \propto$ Mw of blend composition**



# NEW APPROACH TO MOISTURE MANAGEMENT

## GENERIC MOBILITY MAP WITH ISO-FUNTIONALITY CONTOURS

## MOBILITY = FREE VOLUME + LOCAL EFFECTIVE VISCOSITY

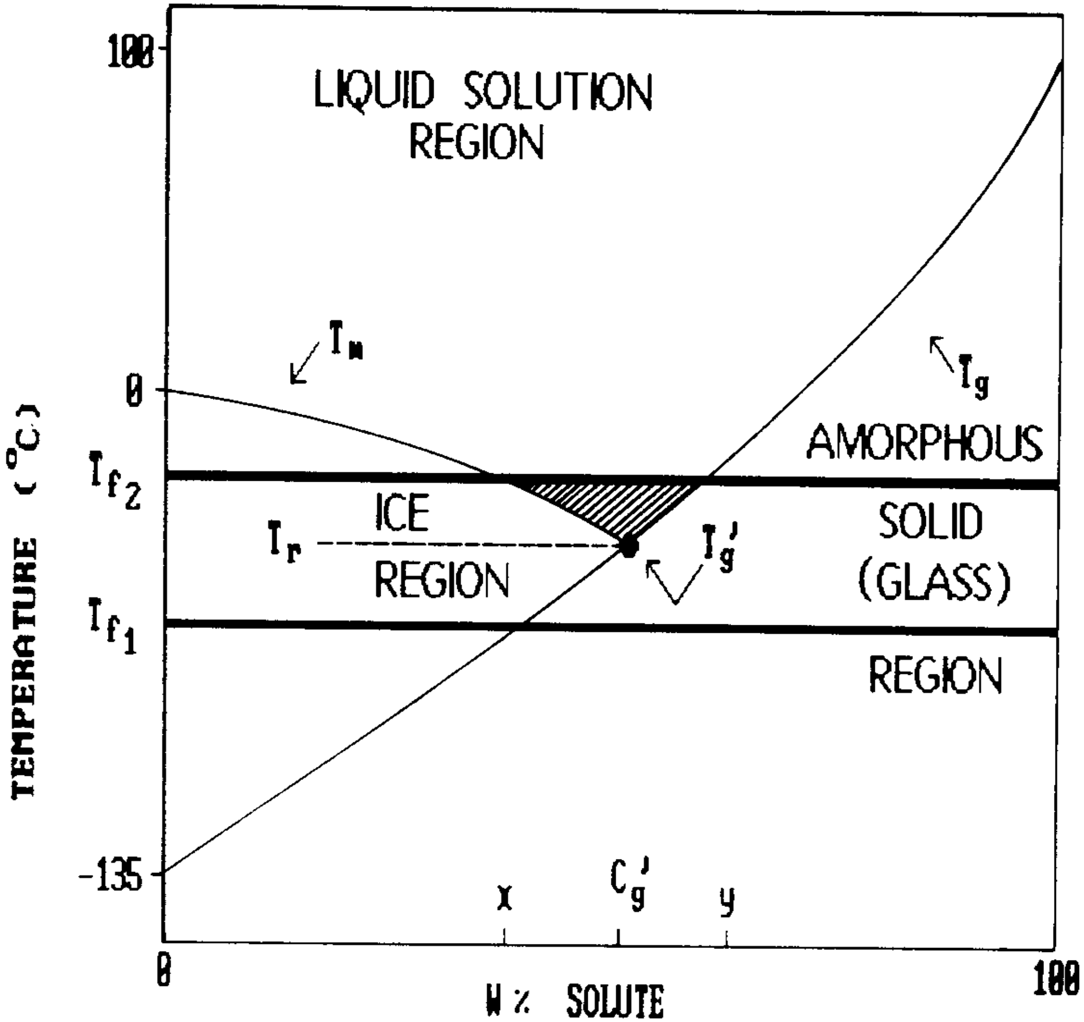


# Cryotechnology of Frozen Foods

## Freezing = Dehydration

FREEZER $T_{f1} < T_g'$ STABLE STORAGE

FREEZER $T_{f2} > T_g'$ PRODUCT DETERIORATION




**Optimum freezer temperature is below or very near above Tg'.**

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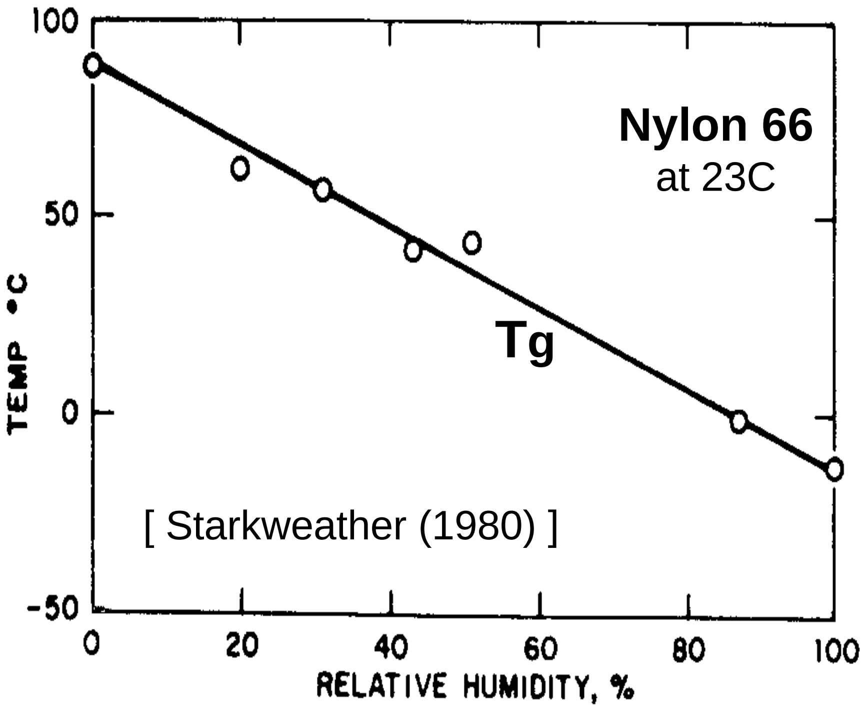
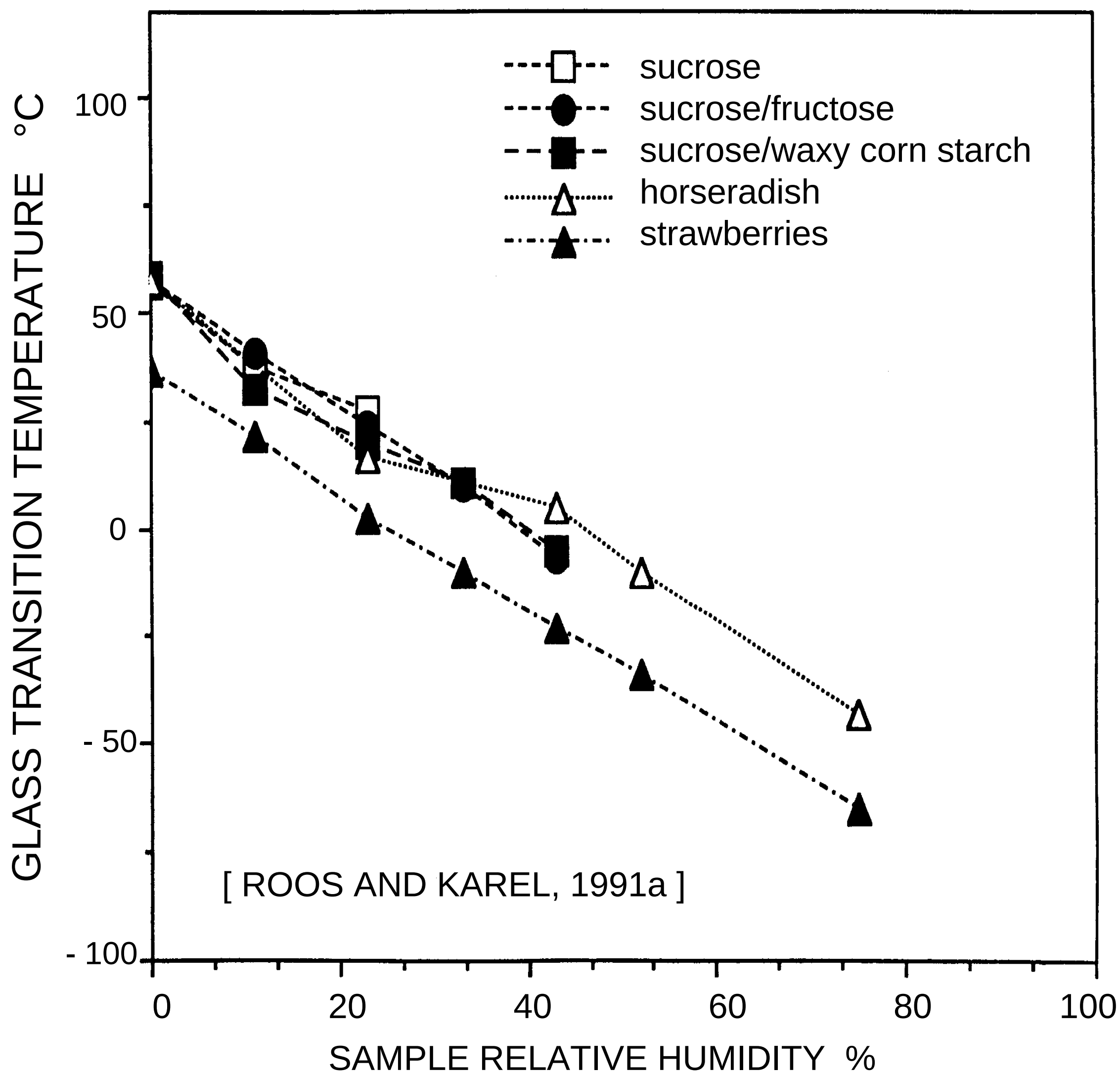
# SAMPLE RH IS LINEAR WITH Tg,
## NOT WITH MOISTURE CONTENT

**For synthetic polymers** **and** **Amorphous food materials**




**APPLICATION: edible barrier films based on food proteins**

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# MOISTURE MANAGEMENT

**3 REGIMES     CONTROL**

**HYDRATION   DRYING   FREEZING   PRODUCT RH**

**MOISTURE MIGRATION   BIOLOGICAL STABILITY**

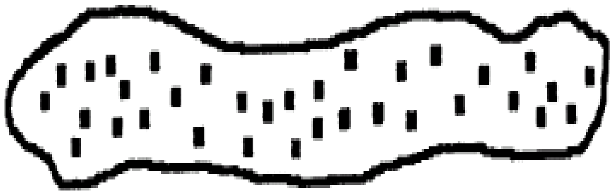
**Scott (1953)** Related *S. aureus* growth at 30°C to "Aw"

Controlled rvp with sucrose; growth when rvp = 0.88 with ~ 62 % sucrose

no growth when rvp = 0.86 with ~ 67.5% sucrose

Tg = Tg' = - 32°C ~ 64 % sucrose

## III T >> Tg

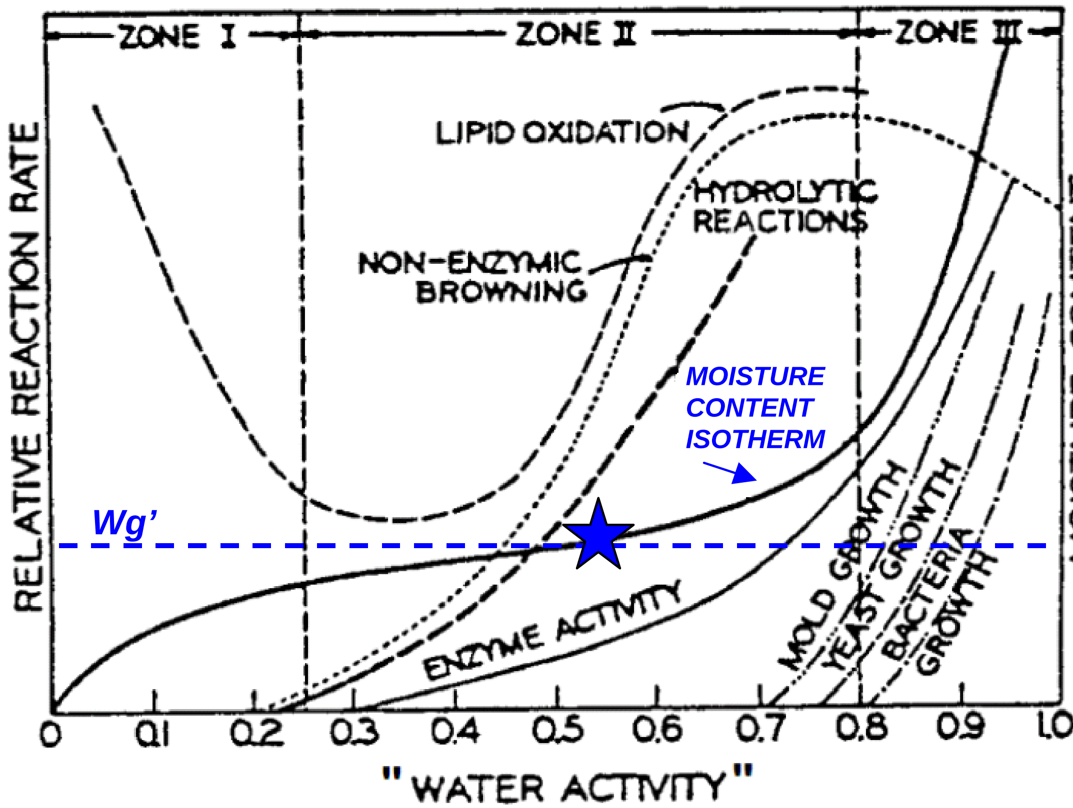


**rvp predicts BOTH surface and bulk moisture loss**

## HOW TO INTERPRET 3 ZONES OF GENERIC SORPTION ISOTHERM

**Labuza Food Stability Map 20°C**

**T << Tg | T<Tg *T~Tg* T>Tg | T >> Tg**

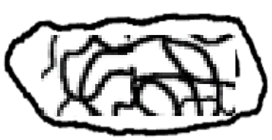


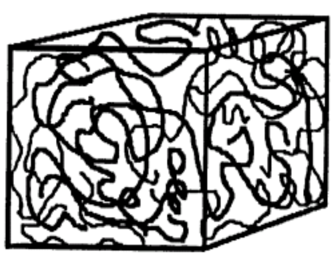

## II T<Tg *T~Tg* T>Tg

**rvp predicts ONLY surface evaporation NOT bulk moisture loss**

## I T<<Tg

*but* $T_{g_{network}}$ > T > Tg





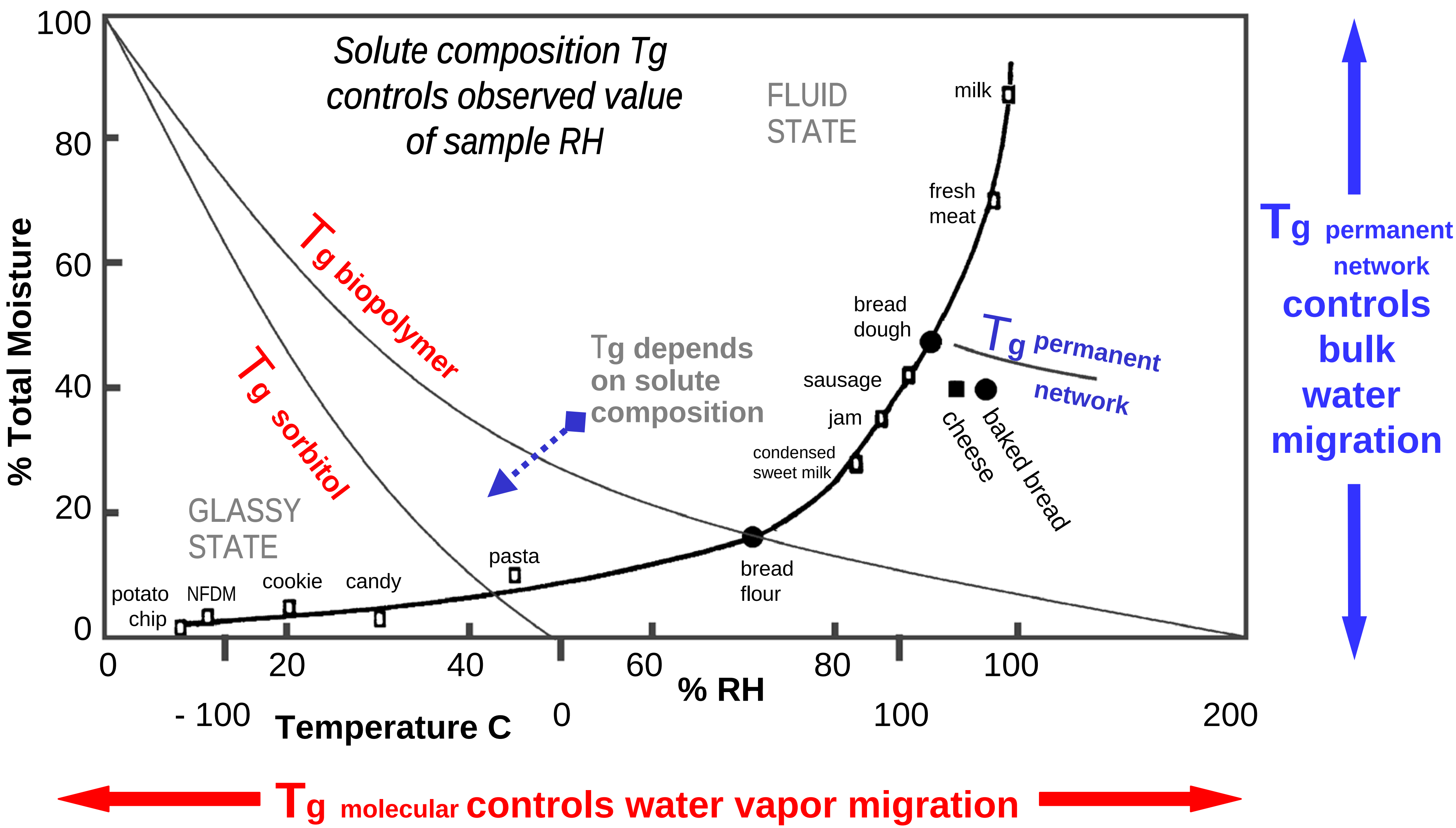
**0** --------------------- rvp = NErvp---------------------------------------------------------- **0.95** rvp ~ Aw **0.995** rvp = mole fxn water concentration **1.0**

NONequilibrium / NONideal — Equilibrium / **NONideal** — Equilibrium / Ideal

100% reference sucrose concentration ~ 43% ~ 6% 0%

# MULTIPLE TEXTURE STABILIZATION REQUIRES CONTROL OF MOISTURE CONTENT, SAMPLE RH, Tg molecular, Tg network

**Bread and cheese are thermoset permanent protein disulfide networks => easy to dehydrate surface, but difficult to remove bulk water content**

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# LEVELS OF S ↔ F RELATIONSHIPS

| | MOLECULAR | ENTANGLEMENT → | SUPRA-MOLECULAR |
|---|---|---|---|
| 1D | **MONOMER**<br>**POLYMER** | | **FIBER** |
| 2D | **FILM** | | **FILM** |
| 3D | **GLASSY MATRIX** | | **GLASSY MATRIX**<br>**NETWORK**<br>**GEL** |

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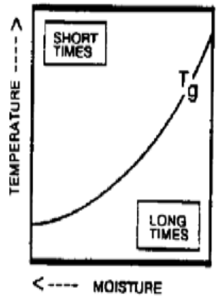
# FOOD POLYMER SCIENCE APPROACH TO INGREDIENT SELECTION




***WATER AT EVERY LEVEL !!!***

| STRUCTURE | FUNCTION | INGREDIENT |
|---|---|---|
| GLASSY MATRIX | MOISTURE MANAGEMENT III<br>MOISTURE MANAGEMENT II | SUGARS<br>SUGAR ALCOHOLS |
| | ENCAPSULATION<br>ICE CRYSTAL CONTROL<br>EXTRUSION HALF-SNACKS<br>SOFT vs HARD<br>SHELF LIFE | SHP<br>DESIGNED HPs BIOTECHNOLOGY<br>POLYDEXTROSE |
| | FAT BLOOM | FATS |
| FILM | PUFFING<br>MICROWAVE HALF-SNACKS<br>VACUUM FRYING<br>CRISPNESS<br>ADHESION / COHESION<br>EXTENSIBILITY<br>ENHANCE COOKIE SPREAD<br>ENHANCE STACK HEIGHT | STARCH AMYLOPECTIN<br>GLUTEN GLIADEN*<br>CASEINATE<br>GELATIN<br>EGG WHITE<br>WHEY<br>CHEMICAL LEAVENERS |

| STRUCTURE | FUNCTION | INGREDIENT |
|---|---|---|
| | MOISTURE MANAGEMENT I | SOY |
| FIBER | REINFORCEMENT<br>SHREDDING<br>MOUTHFEEL<br>TOUGHNESS<br>CRUNCHINESS | STARCH AMYLOSE<br>GLUTEN GLUTENIN*<br>CASEINATE<br>GELATIN |
| NETWORK | MOISTURE MANAGEMENT III<br>RUBBERINESS<br>ELASTICITY<br>RETARD COOKIE SPREAD<br>MAINTAIN STACK HEIGHT<br>DRYING<br>POROSITY<br>EXTEND BOWL LIFE<br>EXTEND SHELF LIFE | STARCH<br>MIRAGEL<br>GLUTEN*<br>CELL WALL POLYMERS<br>PENTOSAN *<br>BETA GLUCAN<br>COCOA* |
| GEL | GELATION | STARCH*<br>GELATIN<br>PENTOSANS*<br>GLUTEN *<br>CASEINATE<br>EGG WHITE<br>SOY |

FOR REDUCED CHOs

RESISTANT STARCHES

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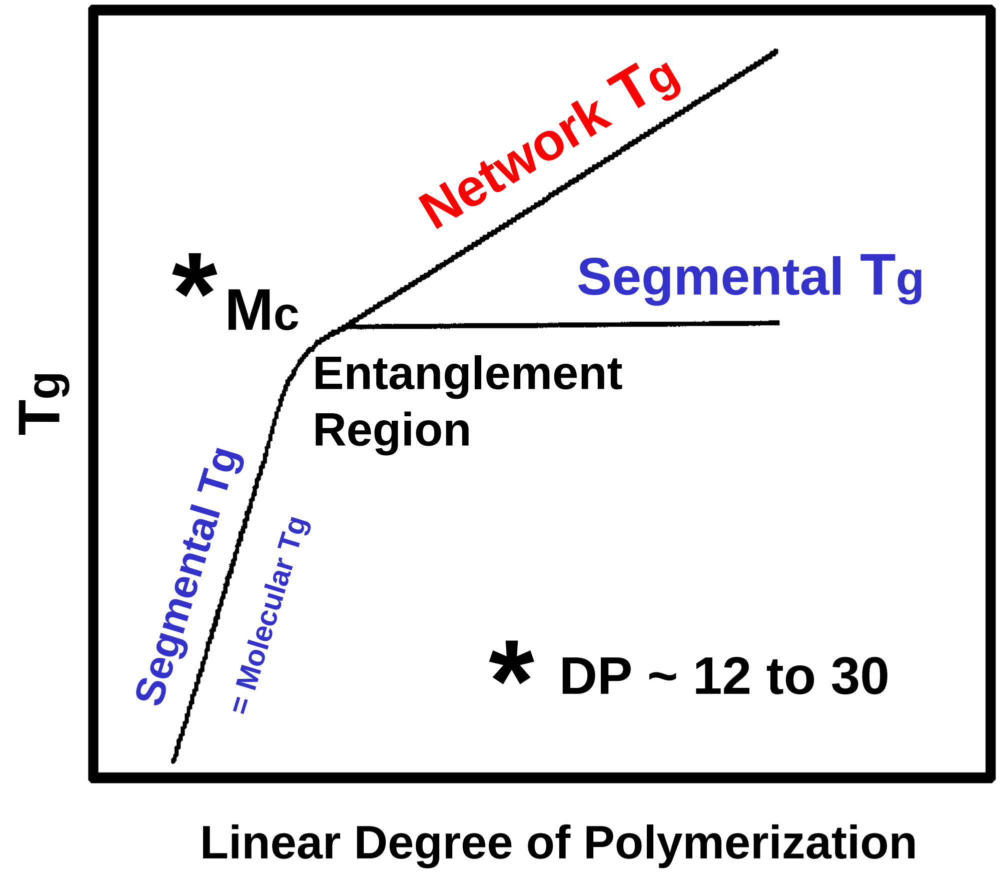
# Segmental vs Supramolecular
# Structure - Function Relationships

**Oriented polymer system model for uniaxially stretched gluten films: network reinforced by anisotropic fibrils**

( Research & Development, October 1988 )

**SEGMENTAL Tg constant above Mc**
**BUT**
**NETWORK Tg continues to increase**




**DESPITE THE COMPLEXITY OF THE HEXAPLOID WHEAT GENOME FOR GLUTEN PROTEINS ----**
**POLYMERIZATION OF GLUTENINS TO MACROPOLYMERS AND ASSOCIATION AS FIBRILS AND NETWORKS PREDOMINATE OVER GENETICS AS DETERMINANTS OF DOUGH STRENGTH**

COLIN WRIGLEY CFW 48:261 2003

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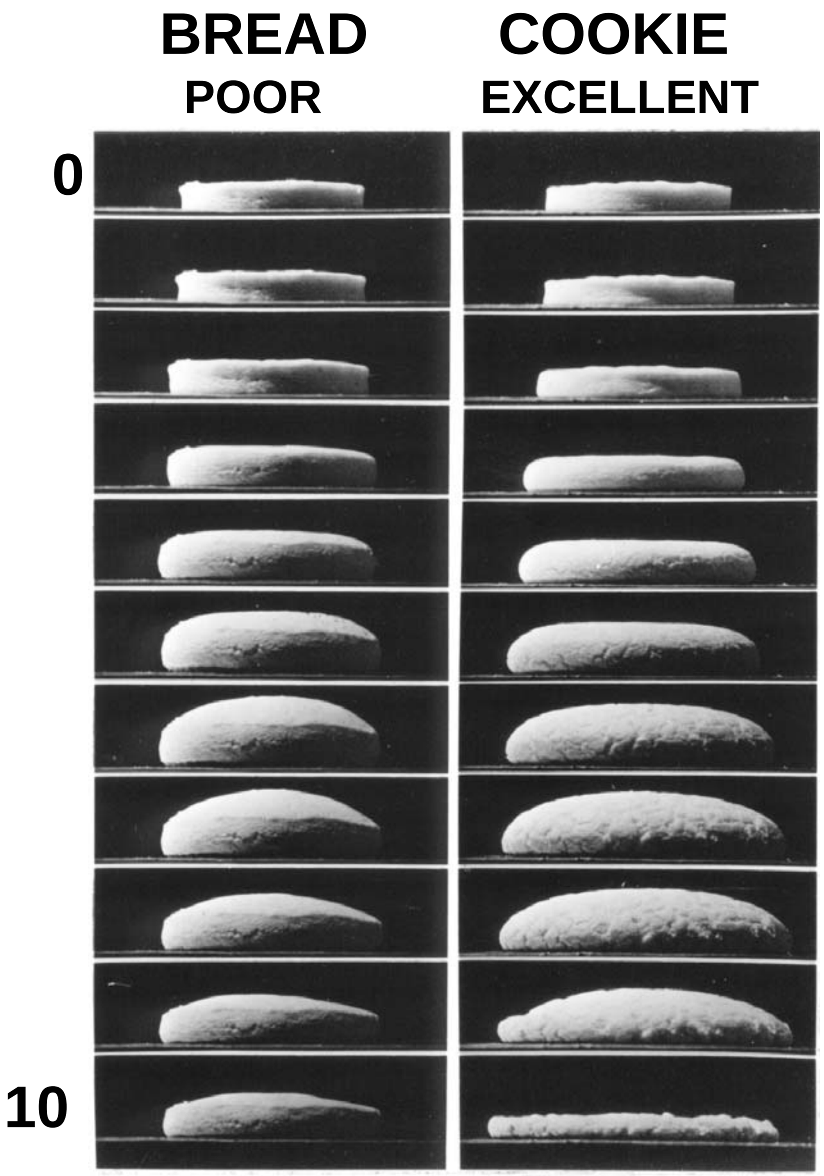
# COOKIE BAKING MECHANISM

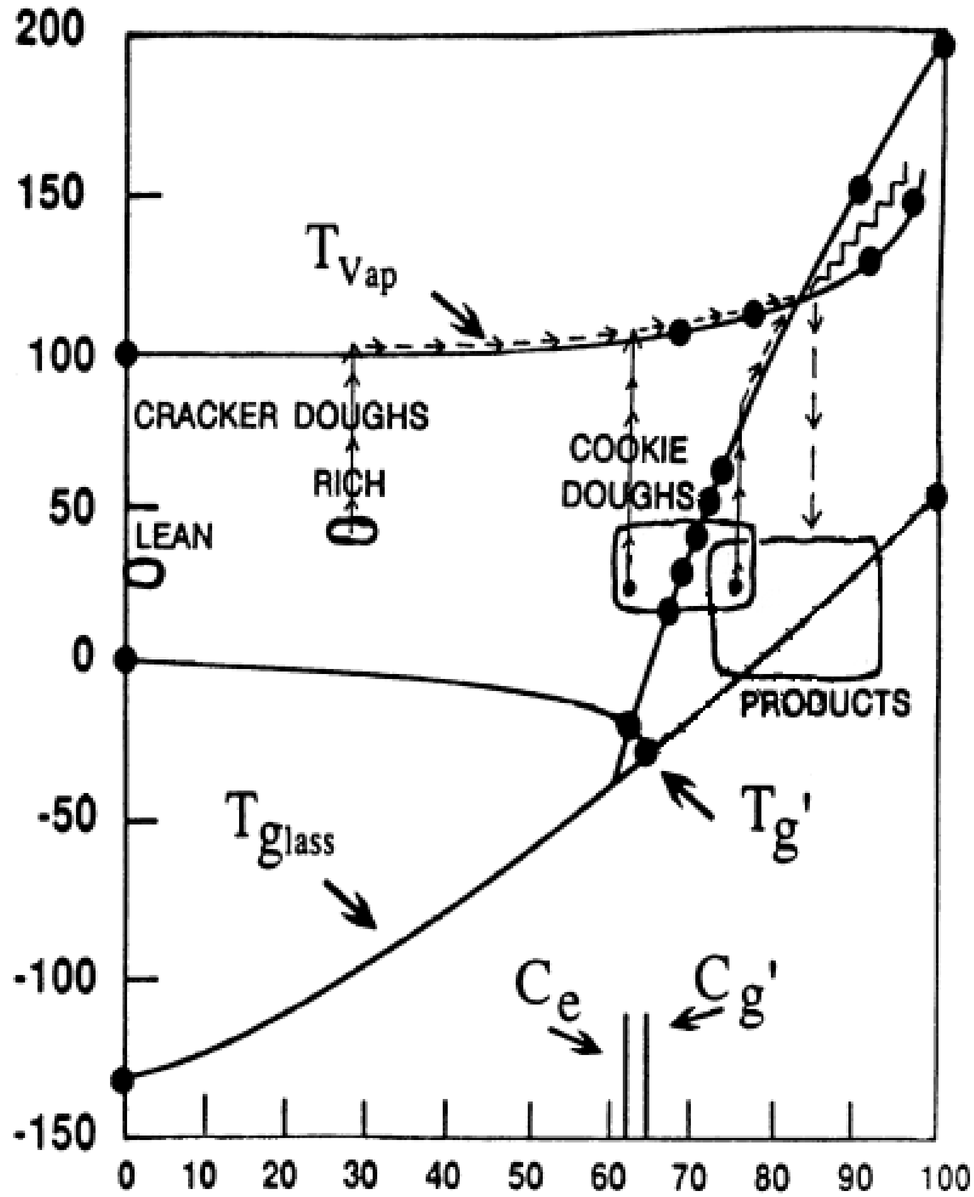
## EFFECT OF FLOUR TYPE



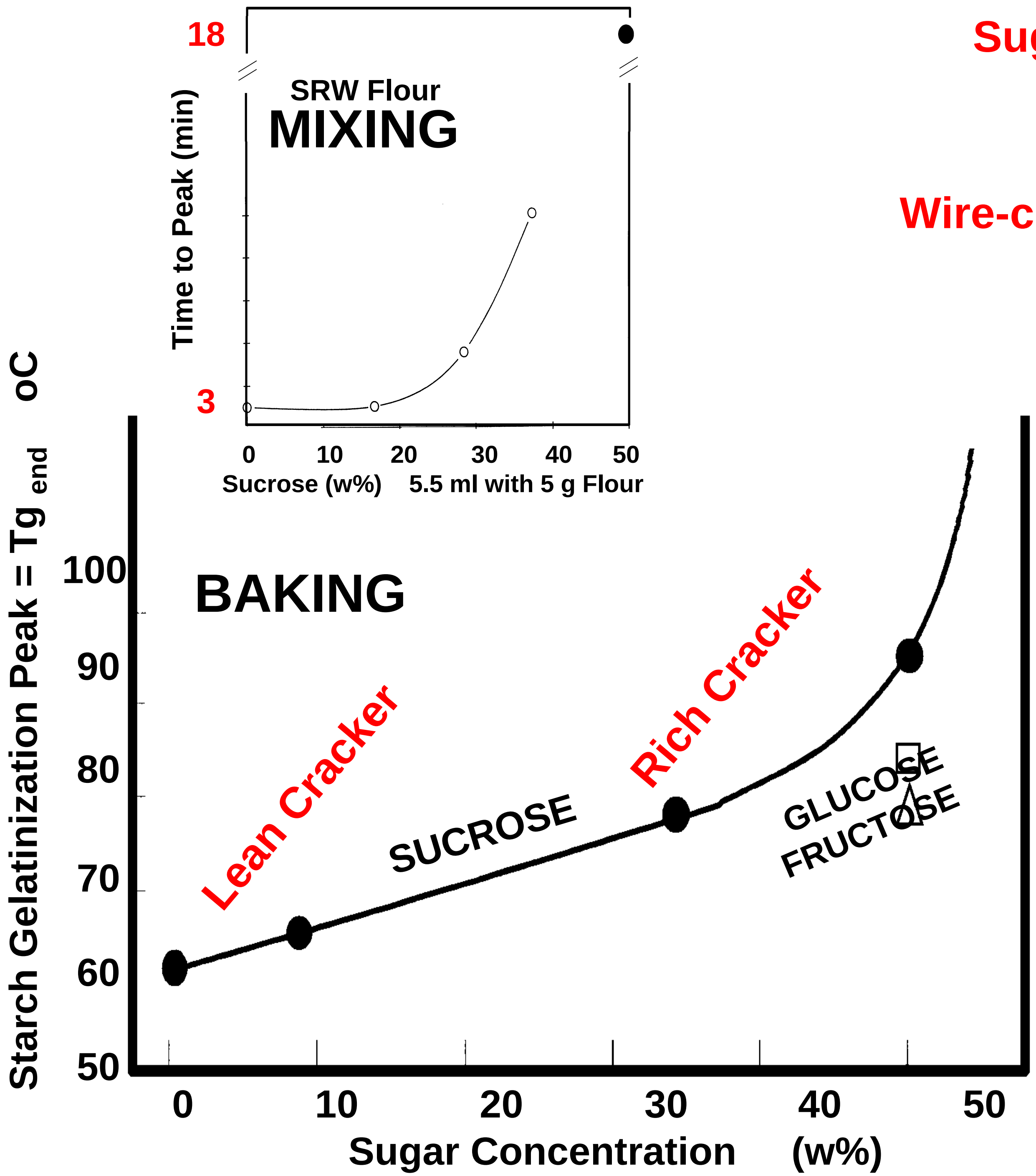

BAKING TIME (min)

## EFFECT OF SUGAR CONCENTRATION

EXTENDED SUCROSE STATE DIAGRAM
AS A BISCUIT BAKING FUNCTIONALITY MAP



# EFFECT OF SUGAR CONCENTRATION




Sugar Snap Cookie AACC 10-52
74 - 80%

Wire-cut Cookie AACC 10-53
~ 67%

# KINETICS

OF MIXING < 50°C

OF BAKING > 50°C

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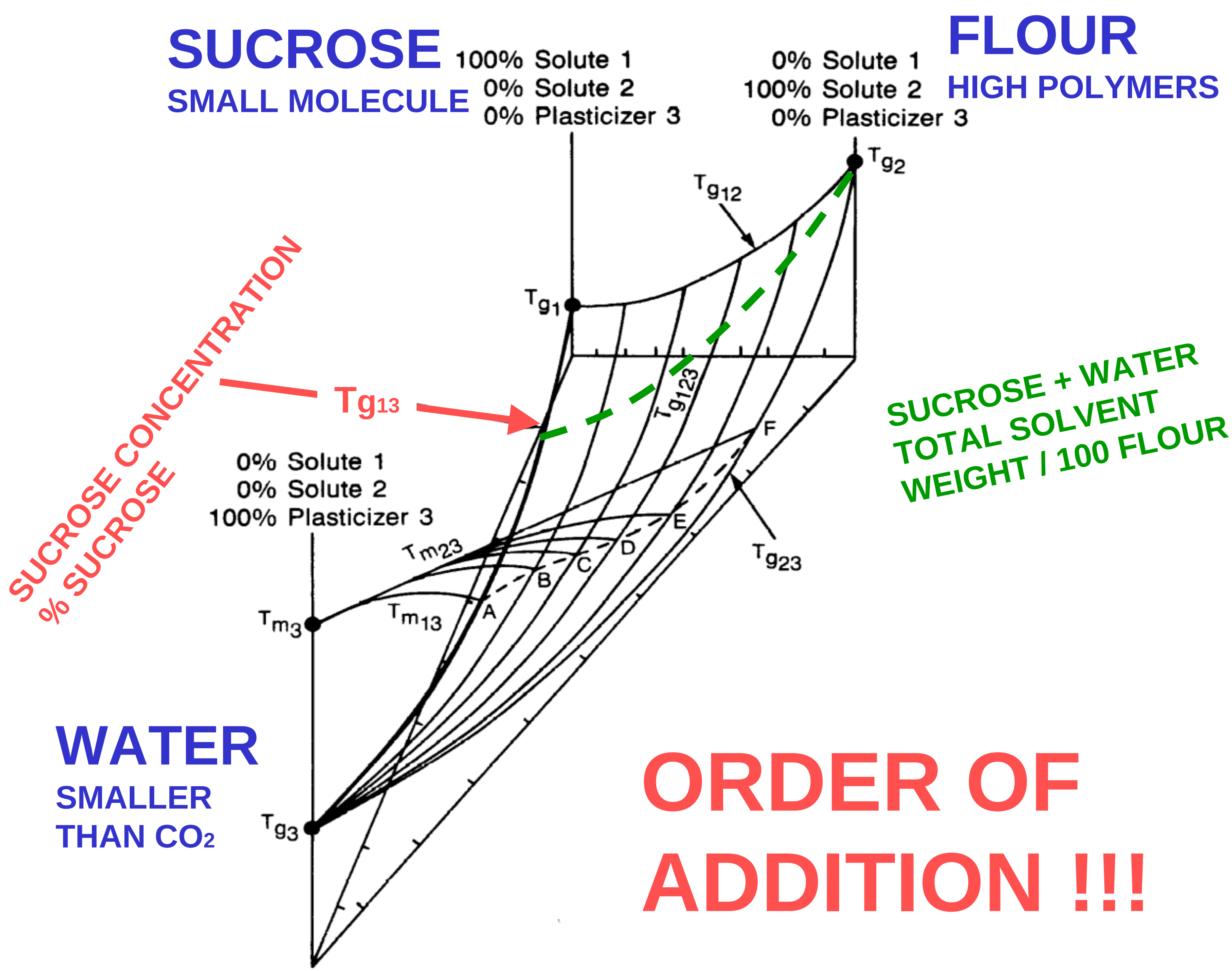
# 3D STATE DIAGRAM AS FUNCTIONALITY MAP FOR COOKIE BAKING




## ORDER OF ADDITION !!!

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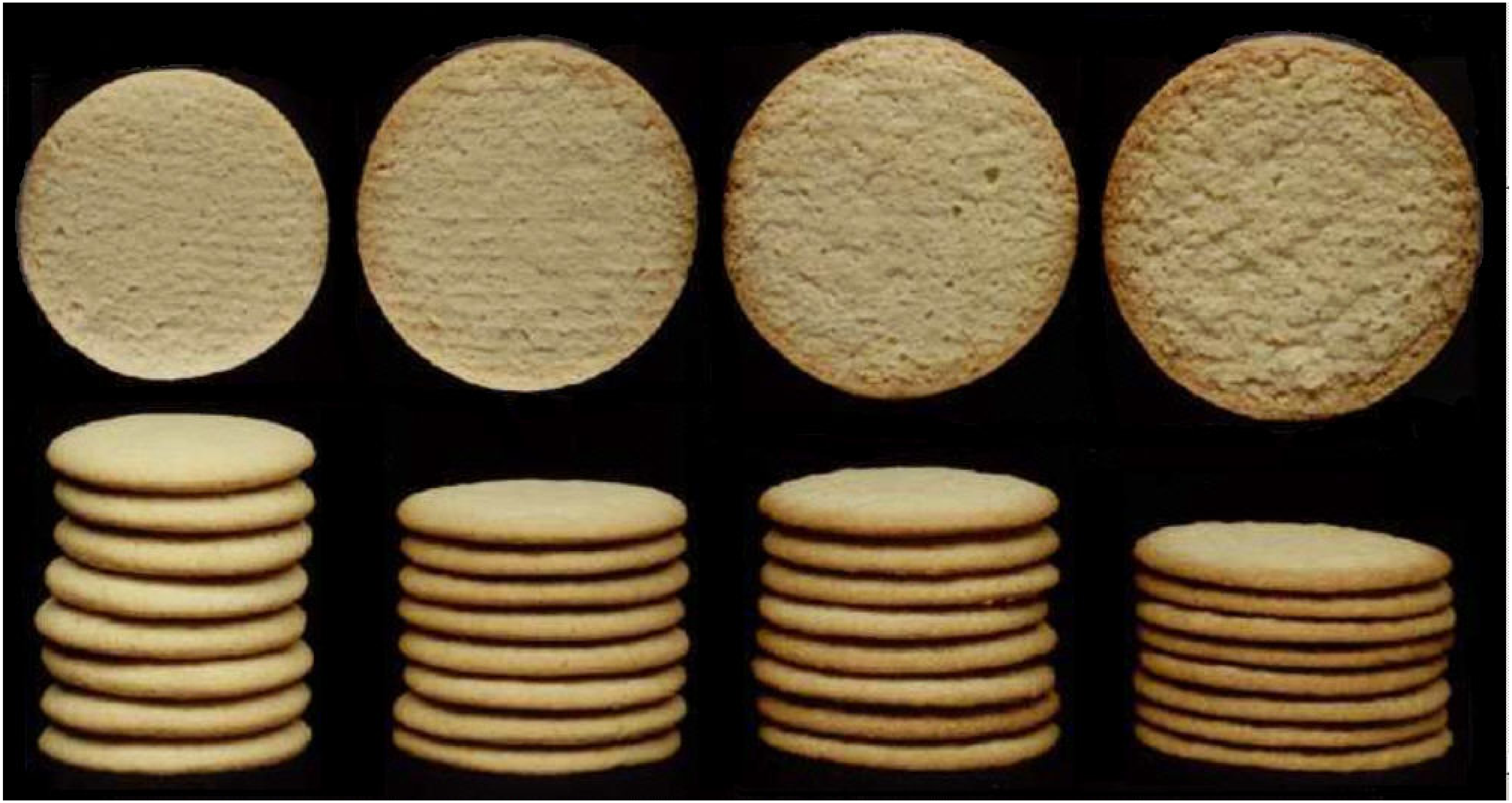
**AACC 10-53**
**Wire Cut Model**

**AACC 10-52**
**Sugar Snap Model**



| | | | | |
|---|---|---|---|---|
| Sucrose | 40 | 45.54 | 52.7 | 60 |
| Water | 23 | 17.46 | 30.3 | 23 |
| S% | 63.5% | 72.3% | 63.5% | 72.3% |
| TS | 63 | 63 | 83 | 83 |
| $\eta^*$ | 240 | 308 firmest | 94 softest | 156 |

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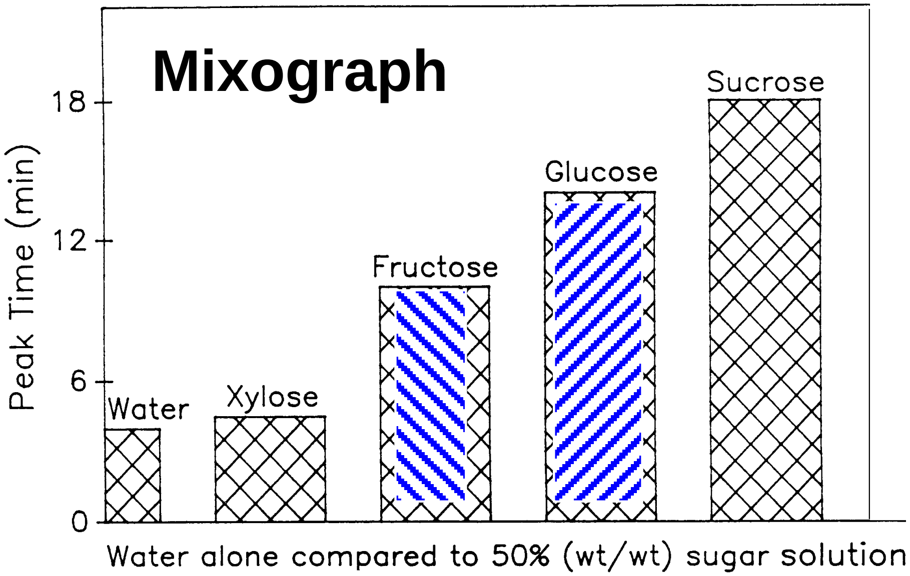
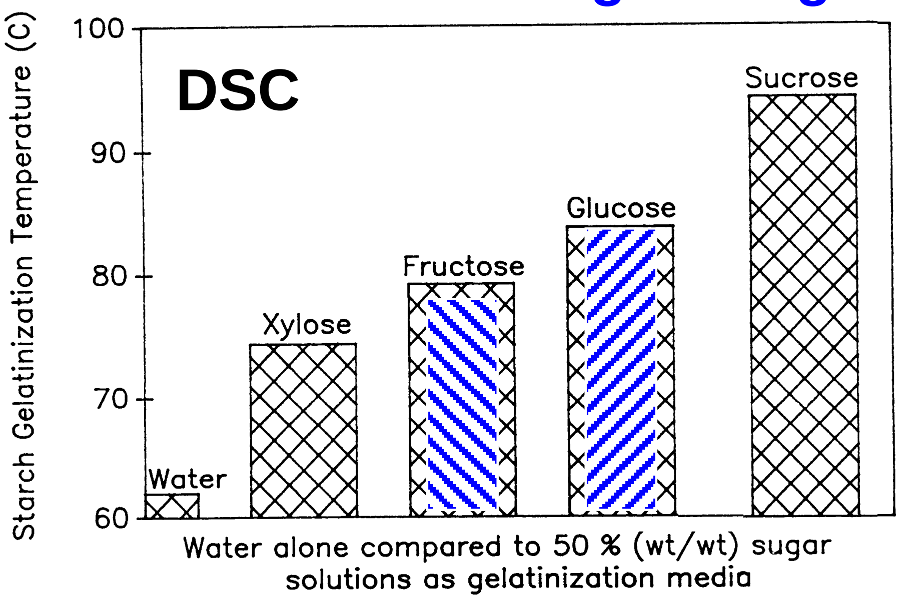
# EFFECT OF SUGAR TYPE

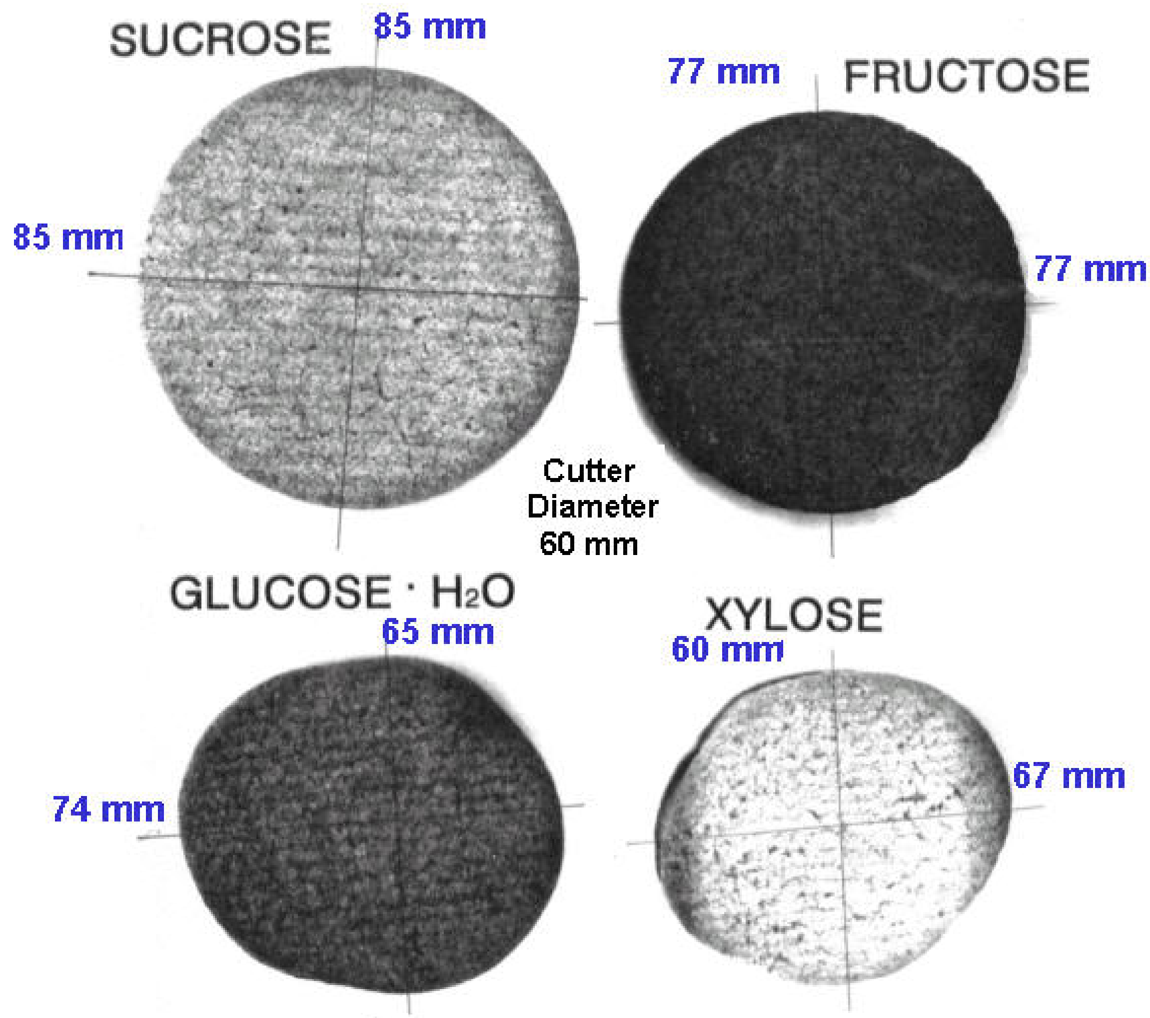
## on gluten during mixing




## on starch during baking




## SUGAR SNAP COOKIE BAKING

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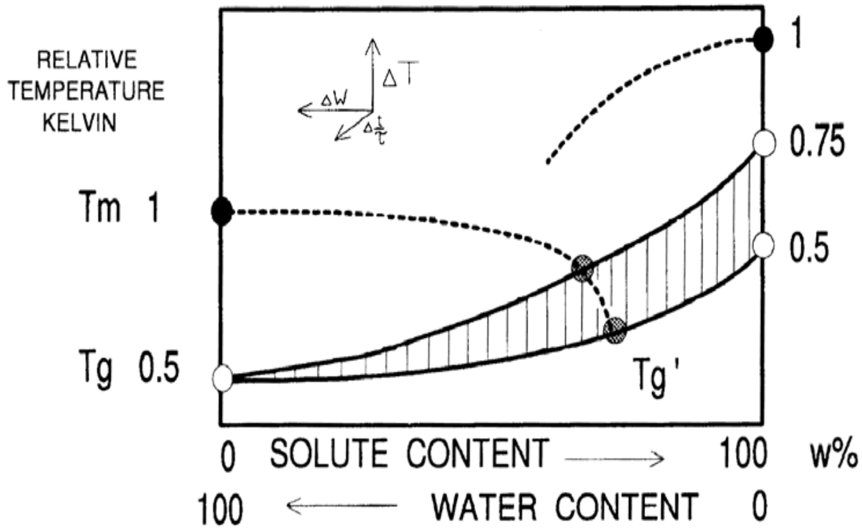
# USE OF MAP TO CREATE SUPERIOR RESISTANT STARCH

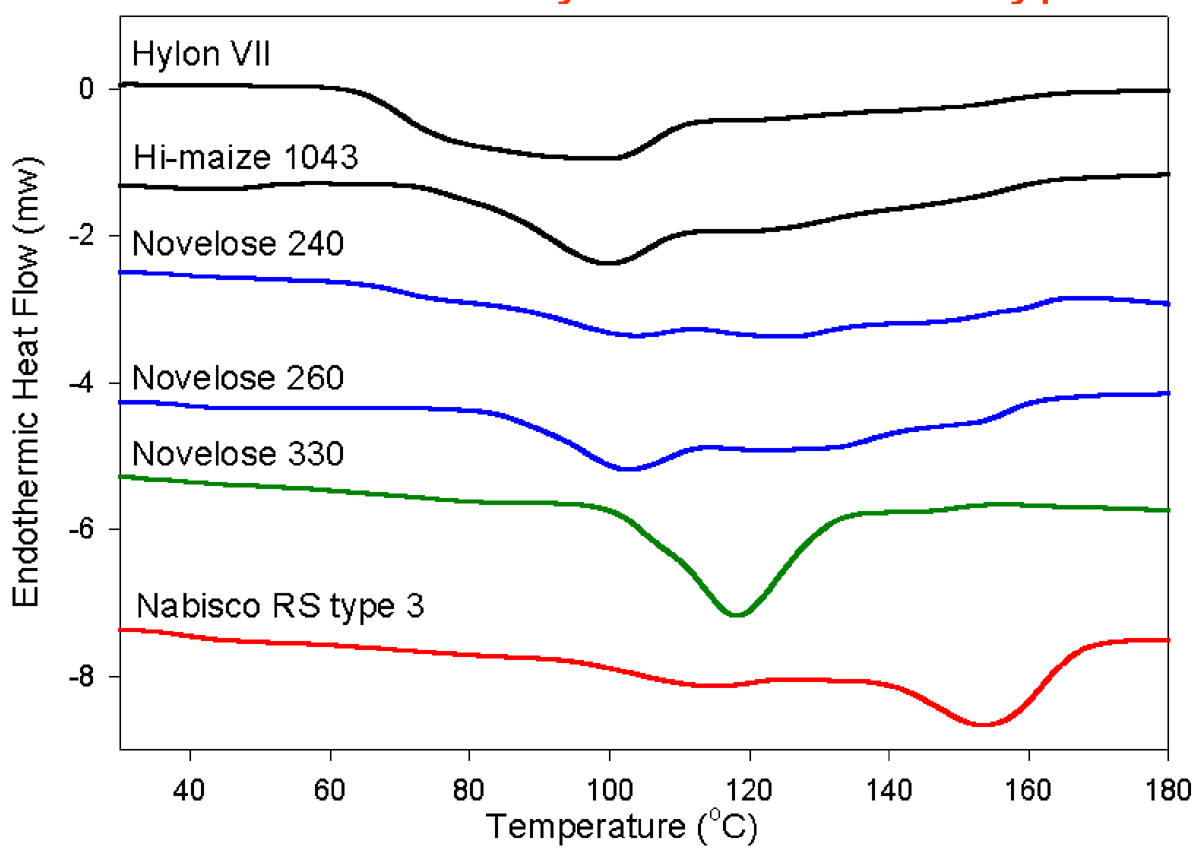
FIND SYSTEM ON t-T-M MAP ISO-FUNCTIONALITY CONTOUR LINES || Tg CURVE




**Target 150C**

**Avoid L-Am**
**110-130C**

Thermal stability of Nabisco RS type 3

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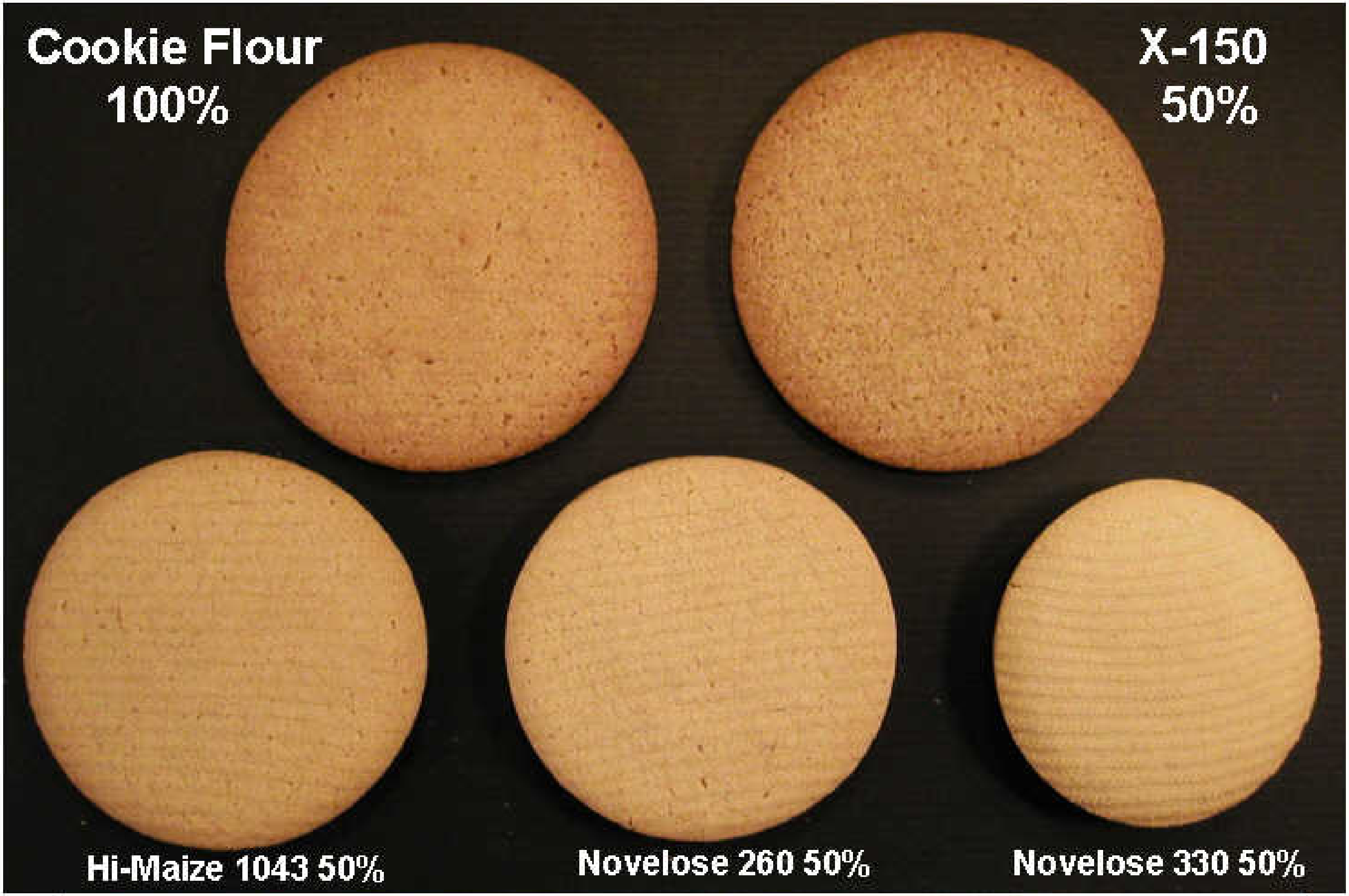
# AACC 10-53 Wire-Cut Cookie Test Baking

## with Cookie Flour Control versus 50% Replacement of Flour by Nabisco Patented X-150 or Commercial Resistant Starch Ingredients




INVERTED SHOULDER

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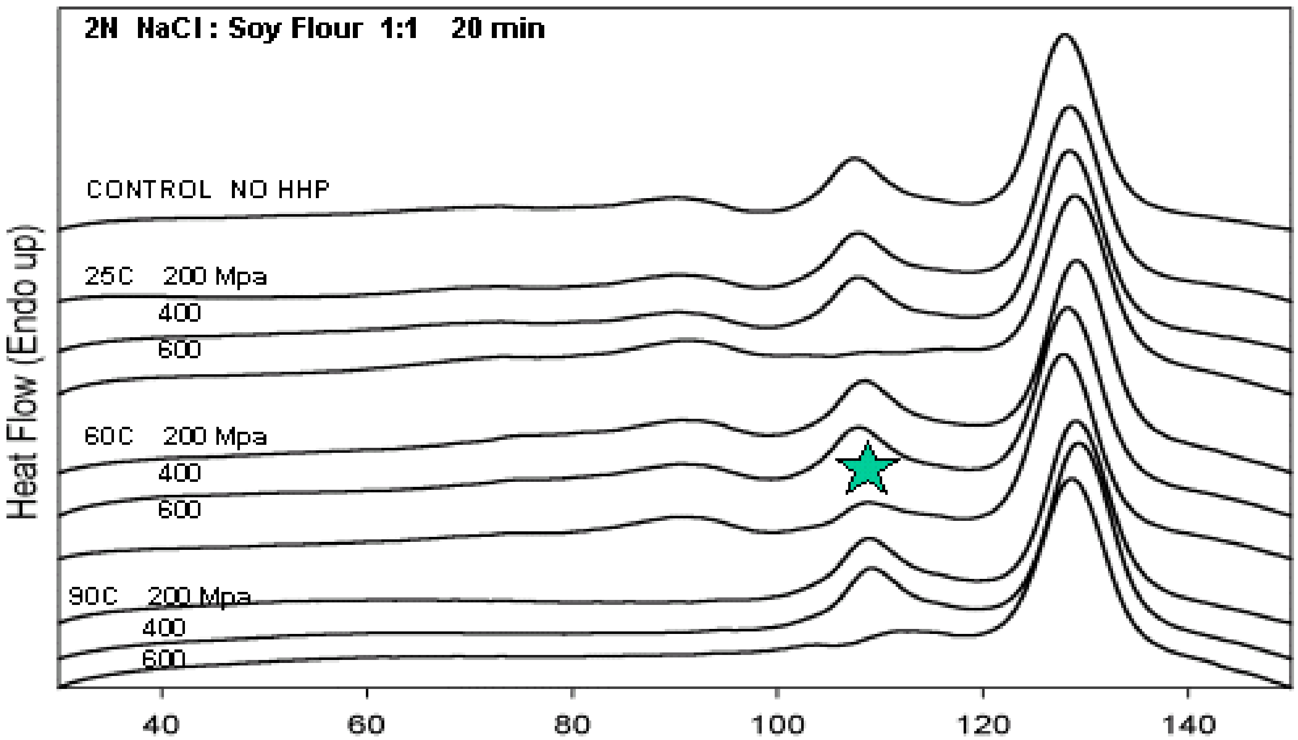


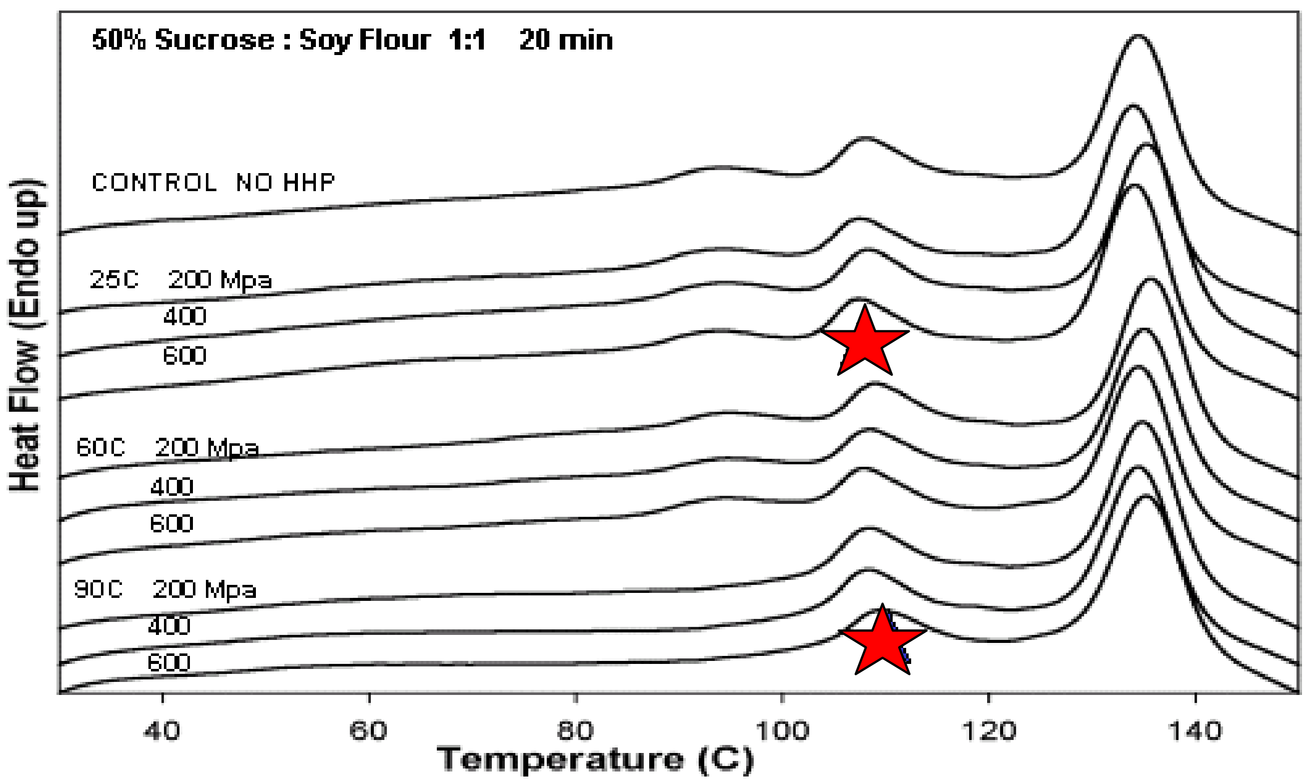


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# 4th DIMENSION

## ENERGETICS

Aqueous salt solution is NOT a glass-forming solvent

## KINETICS

Order of addition effect of glass-forming sugar-water plasticizer blend on soy protein Td ( denaturation peak temperature = end of glass transition region )

## BAROPROTECTION

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# *not so* NEW APPROACH TO FOOD RESEARCH

# *BUT STILL EVOLVING !!*

**(over 75 thesis programs and 2000 publications from industry, government, and academia)**

MOISTURE MANAGEMENT

"WATER ACTIVITY" THEORY OF CONTROL

PROCESS CONTROL STORAGE STABILITY

GLASS TRANSITION EFFECT ON PROCESSING

## FOOD POLYMER SCIENCE

WATER DYNAMICS

GLASS DYNAMICS

**?? to FoodPolymerScience@gmail.com**

**Questions and answers will be collated and sent to everyone**

*LSHL*