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Developing Structure-Process-Property Relationships using Multivariate Analysis

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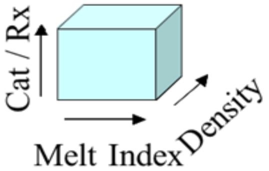
D. M. Fiscus

(David.M.Fiscus@ExxonMobil.com)

Overview

Monomers
Ethylene
Hexene
Butene

Resin Molecular Architecture

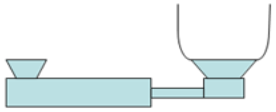


Inter and Intra-Molecular Comonomer Distribution / LCB / Unsaturation

MI and Density, GPC, A-TREF, CFC, SAOS, Rheotense

Forward

Fabrication Process

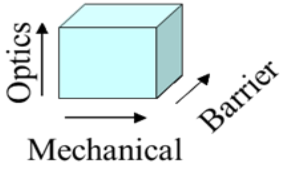


Reverse

Production rate, die gap, blow up ratio, film gauge

Performance

Film

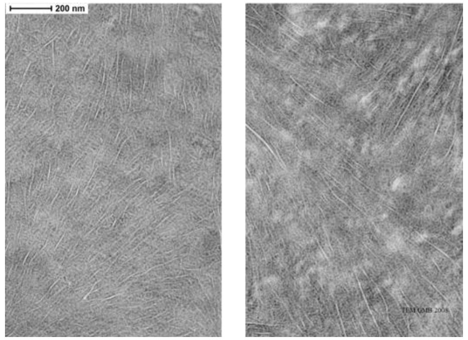


Tensile, Tear and Impact Resistance, Optical Properties

EWF, PLM, Raman, IR

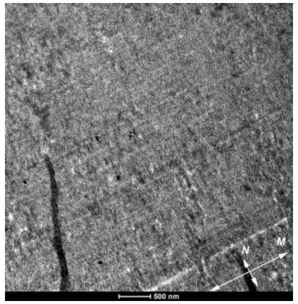
Random Coil

Resin Morphology

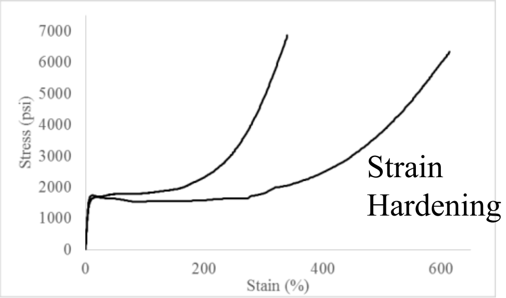


DSC, X-ray, Raman, Solid State NMR, AFM, PLM, IR measure different aspects of resin and film morphology.

Film Morphology



Failure



Strain Hardening

Yield

Plastic Flow

Differences based on micromechanical interpretations of stacked lamella.
Extend to explaining toughness differences, like tear resistance.

Structure-Process-Property Analysis

Molecular Architecture and Morphology

Solution	Melt	Spectroscopic

Melt Index
Density
Additives

GPC
TREF
CFC

ODR
Rheotense
DSC

IR
NMR (^{1}H, ^{13}C, SS)
Raman
X-Ray
PLM

Fabrication Control Variables

Production Rate,
Temp,
Die Gap
Blow-up Ratio
Gauge

Fabrication Quality Variables

Temp,
Pressures
Torque

Part Performance

Engineering:
Tensile,
Tear, Impact,
Optics,
Barrier

Mechanics
(EWF)
Micromech

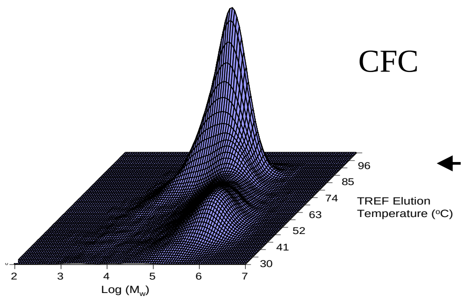
Molecular Architecture / Morphology

Spectroscopic

IR
NMR (^{1}H, ^{13}C, SS)
Raman
X-Ray
PLM

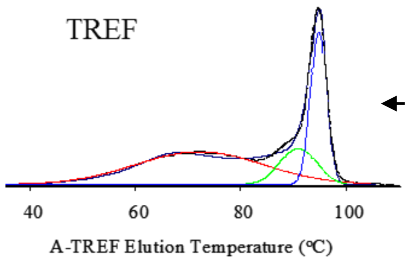
?

CFC

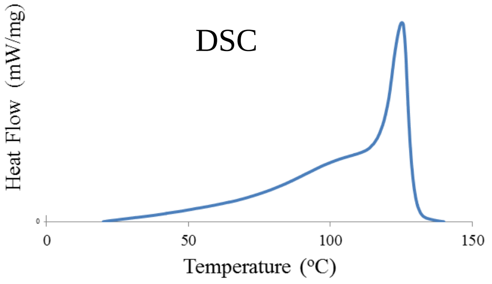


Comonomer Distribution

TREF

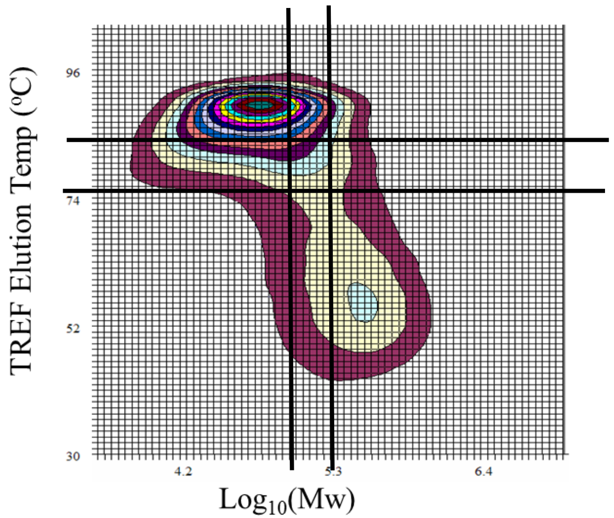


DSC



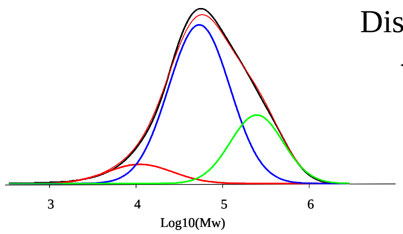
Bin Results

Contour Plot of
Molar Mass / Chemical Composition

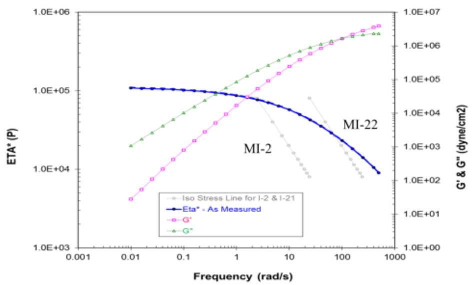


CFC Plot

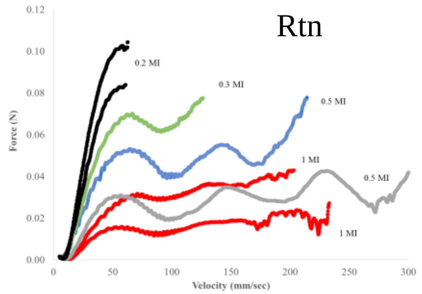
GPC



Molar Mass Distribution



Rtn



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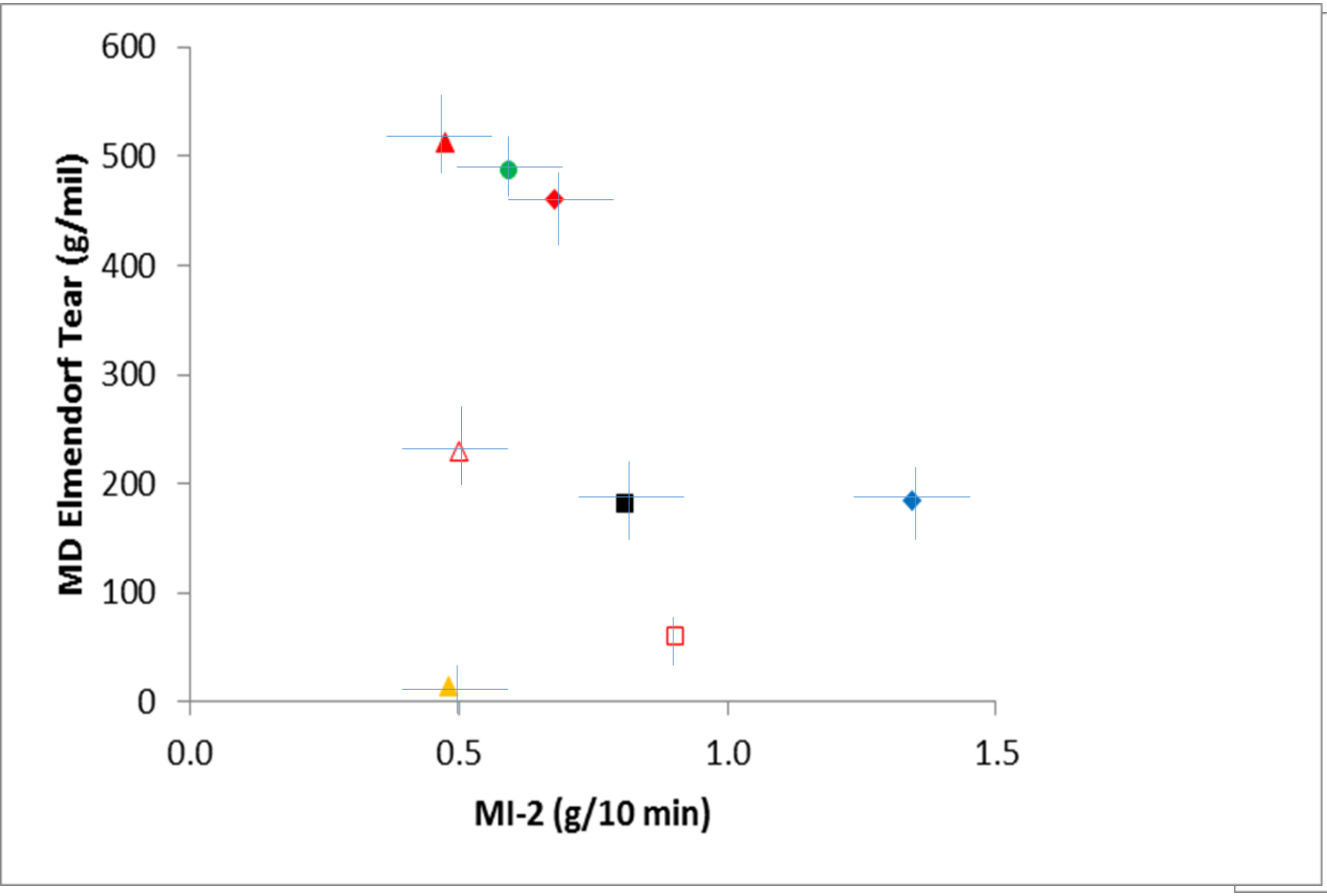
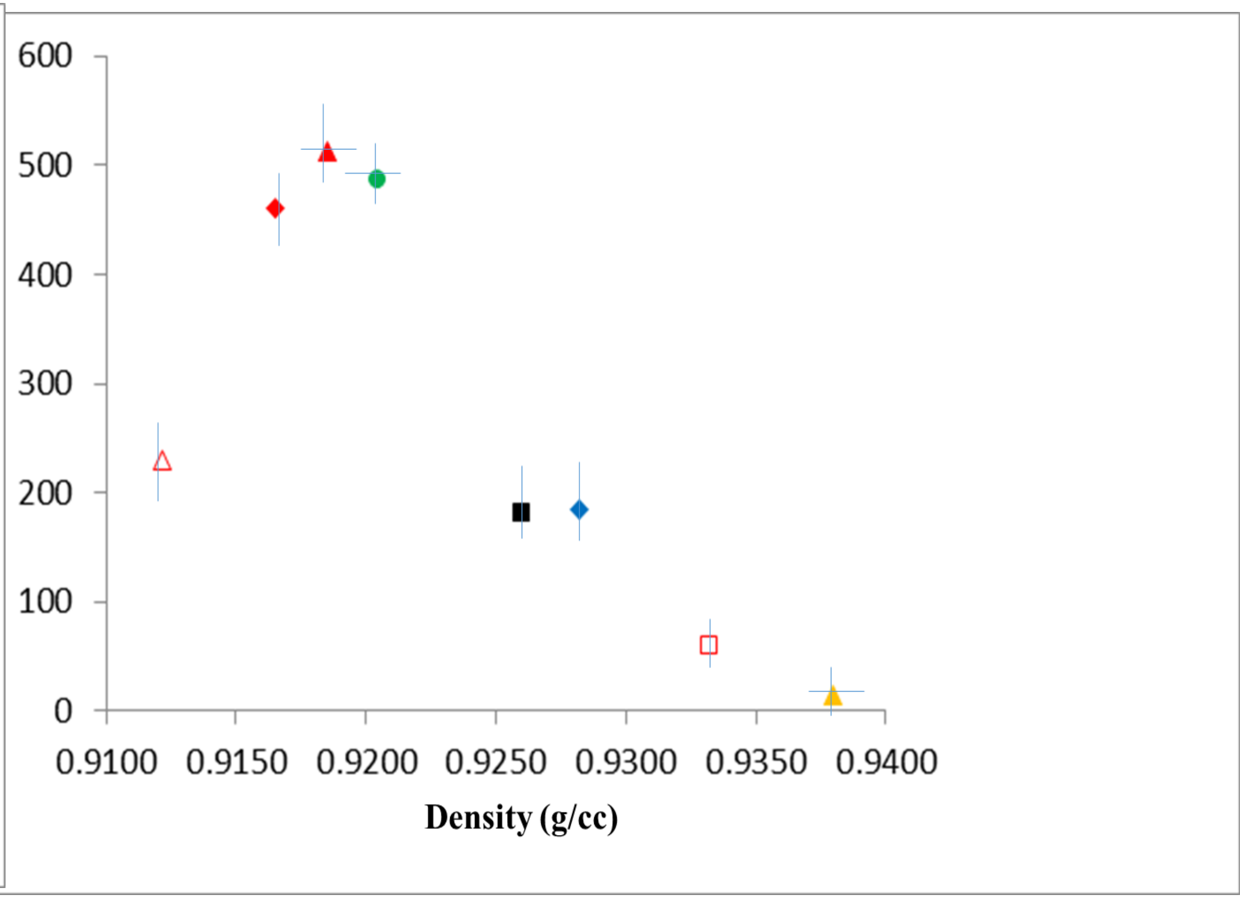
Cross Model   Double Reptation Theory

Univariate Analysis

Relationships use different measurement scales.
Relationships are general and not always monotonic.





Average of selected samples.

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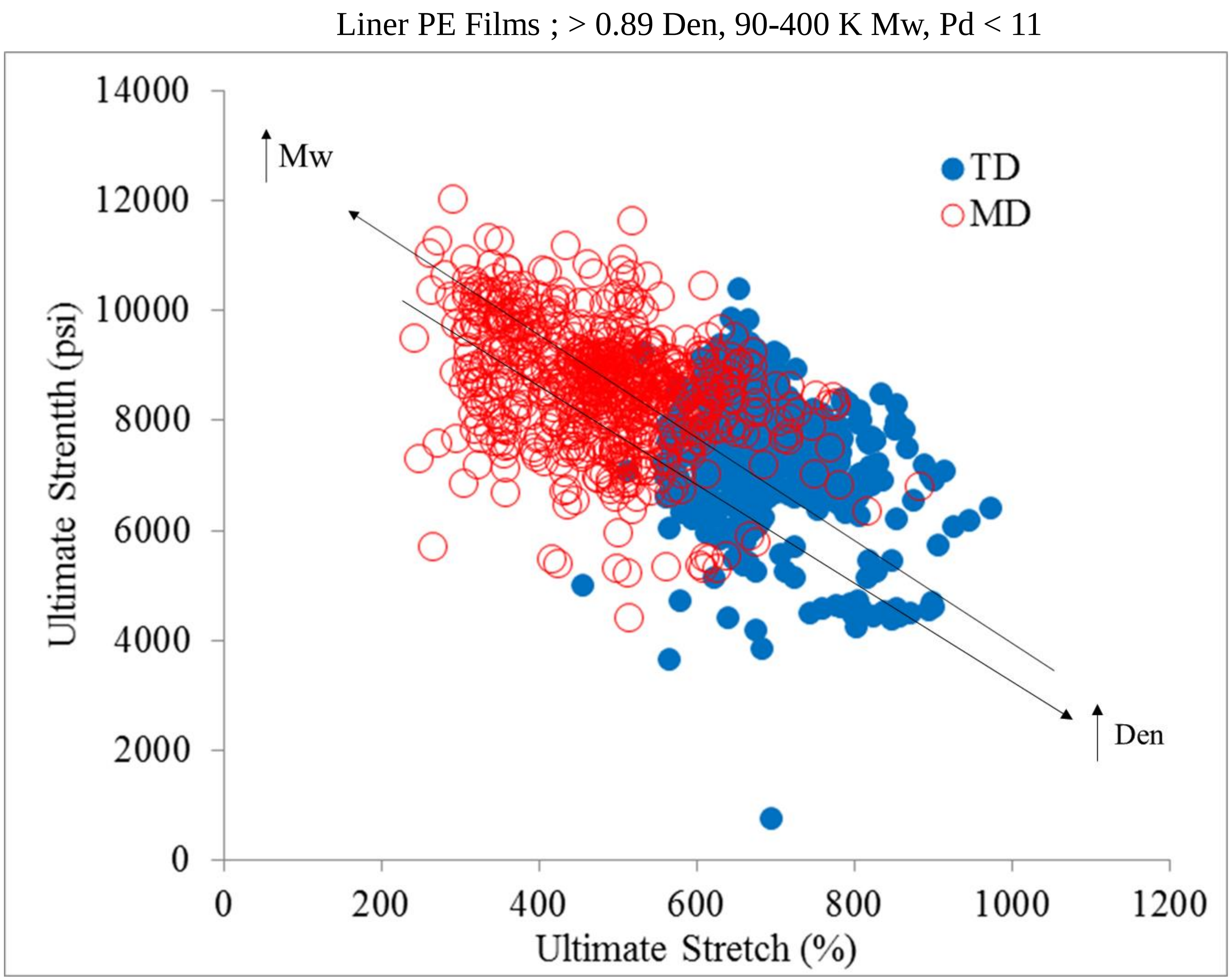
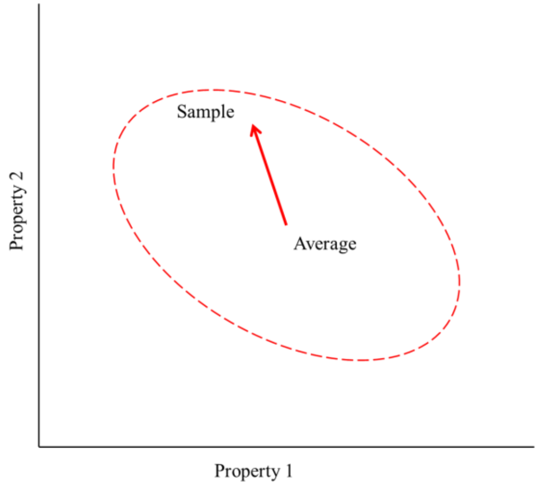
Overlay Plot of Univariate Results





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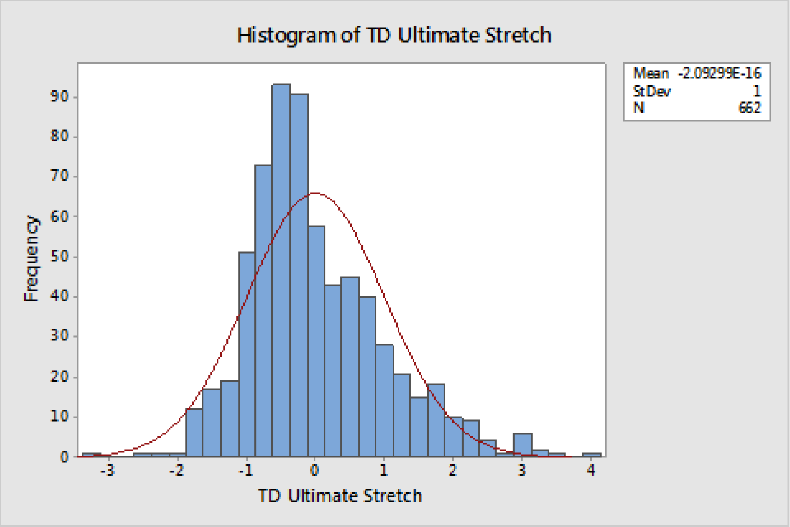
Statistical Analysis

Statistics removes differences due to measurement scales: variable effects are on equal footing.

Statistics describe populations

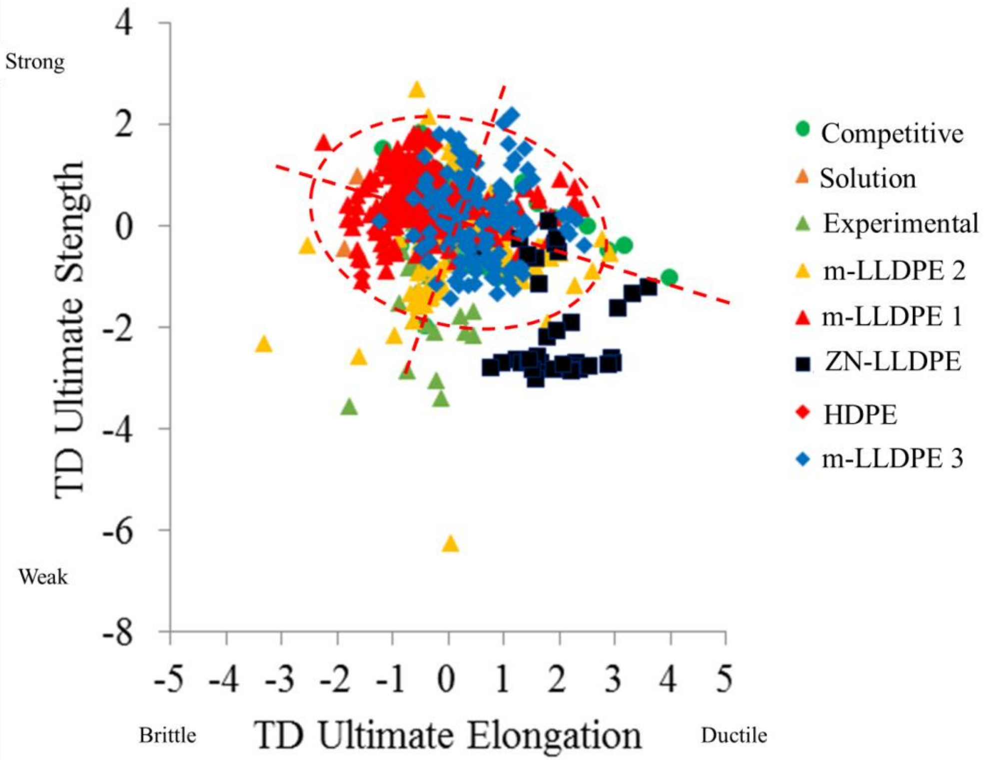
Performance increases with normalized values:
Distance and direction depict performance



Mean ≈ most frequent value
Spread ≈ four standard units of deviation
Values are mean centered and scaled to unit variation.

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

x is the individual data value
μ is the data's average value
σ is the standard deviation



$$f(x) = \frac{1}{2\pi\sigma_1\sigma_2\sqrt{1-\rho_{12}{}^2}} e^{-\frac{1}{2(1-\rho_{12}{}^2)}\left[\left(\frac{x_1-\mu_1}{\sigma_1}\right)^2 + \left(\frac{x_2-\mu_2}{\sigma_2}\right)^2 - 2\rho_{12}\left(\frac{x_1-\mu_1}{\sigma_1}\right)\left(\frac{x_2-\mu_2}{\sigma_2}\right)\right]}$$

x_i is the data's individual values
μ_i is their average values
σ_i is the standard deviation for their average values
ρ_{12} is their coefficient of correlation

$\rho_{12} = \frac{cov(x_1,x_2)}{\sigma_1\sigma_2}$ where $cov(x_1,x_2) = \sum(x_1-\mu_1)(x_2-\mu_2)/(n-1)$
n is the number of paired data points.

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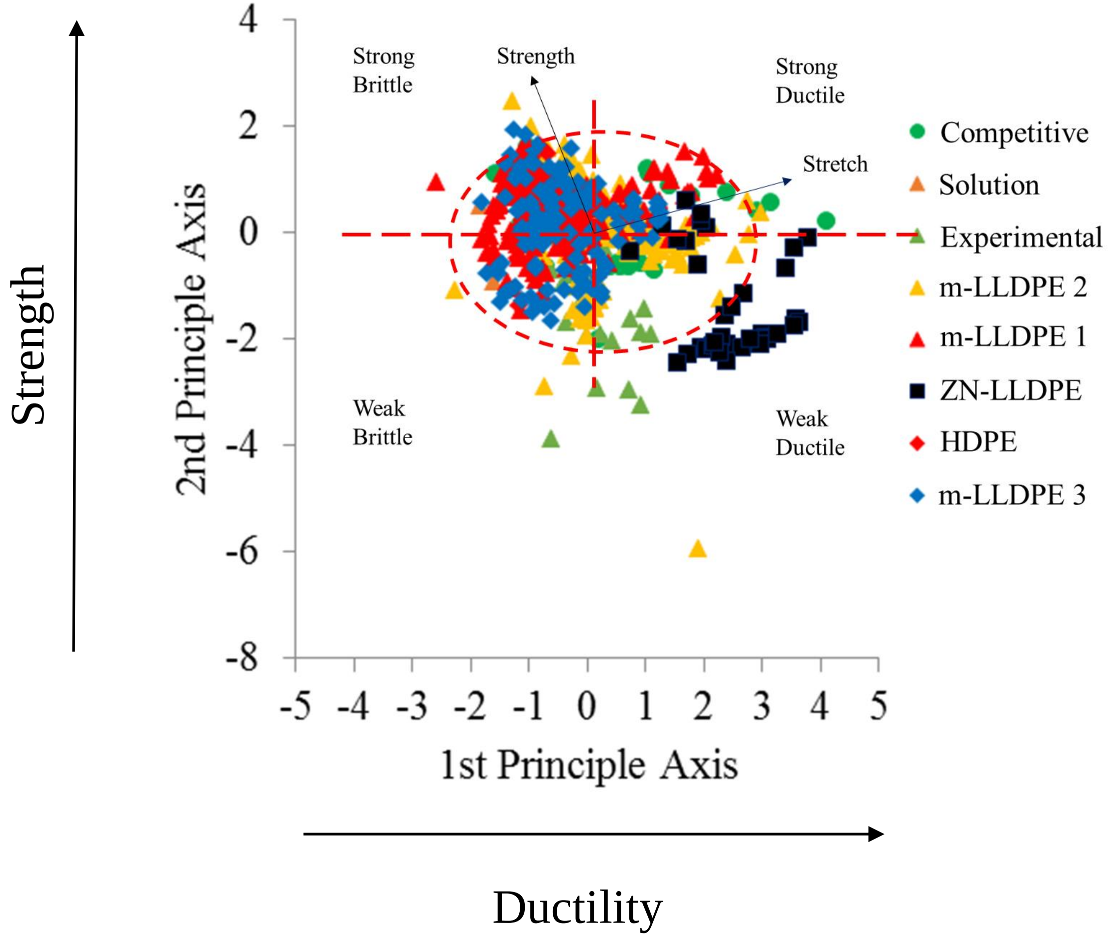
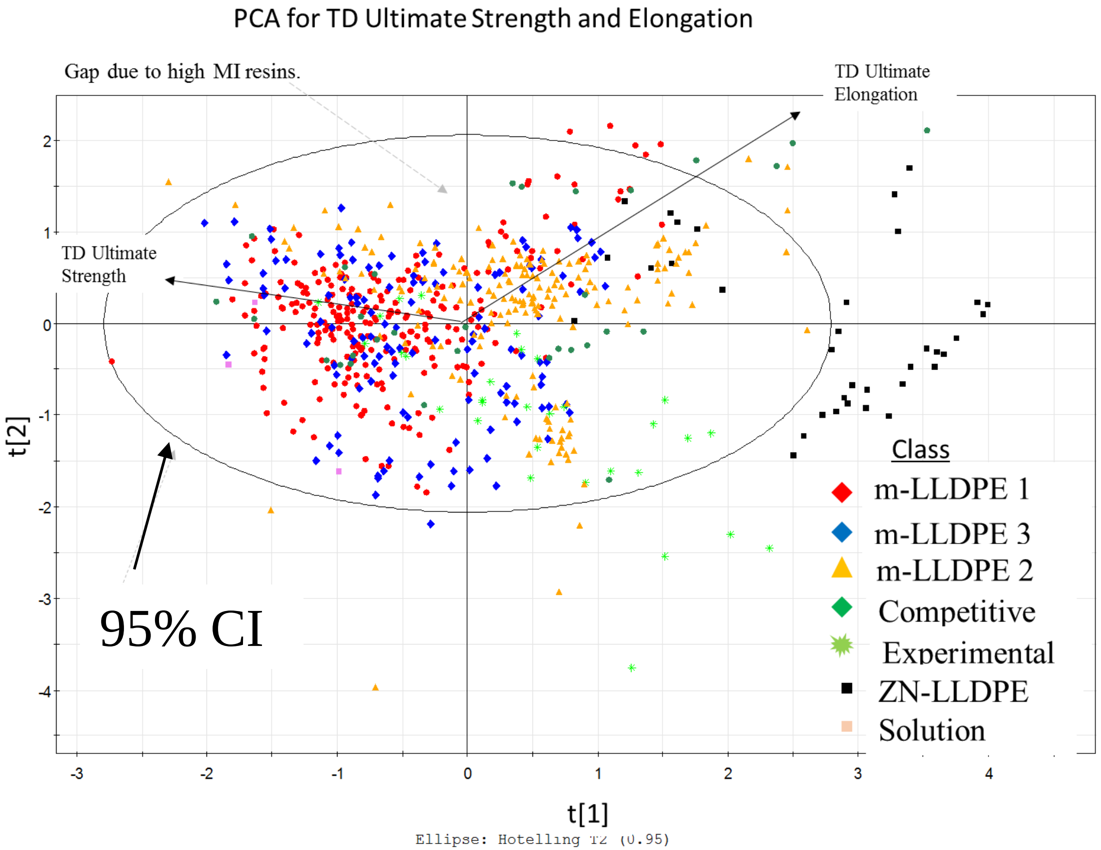
Interaction: How the results of one population are restricted by the value of the other population

Dealing with Covariance

Principle axes reduces covariance.



Orthogonal axes eliminates covariance.



$$f(x) = \frac{1}{2\pi\sigma_1\sigma_2} e^{-\frac{1}{2}\left[\left(\frac{x_1-\mu_1}{\sigma_1}\right)^2 + \left(\frac{x_2-\mu_2}{\sigma_1}\right)^2\right]}$$

x_i is the individual data values

μ_i is their average value

σ_i is the standard deviation for those average values

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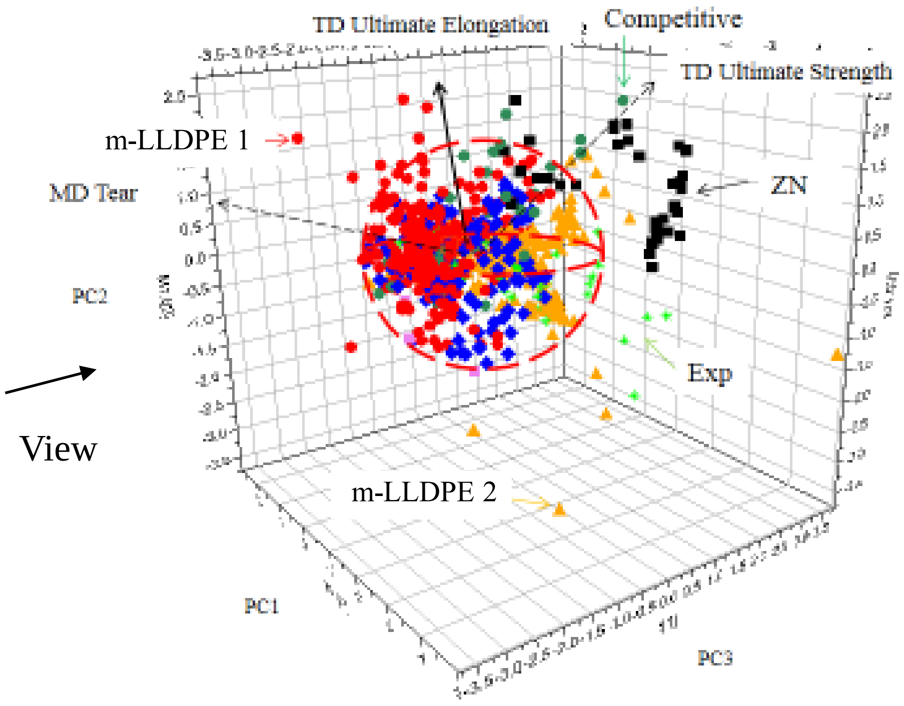
PCA of MD Tear Resistance and TD Ultimate Properties

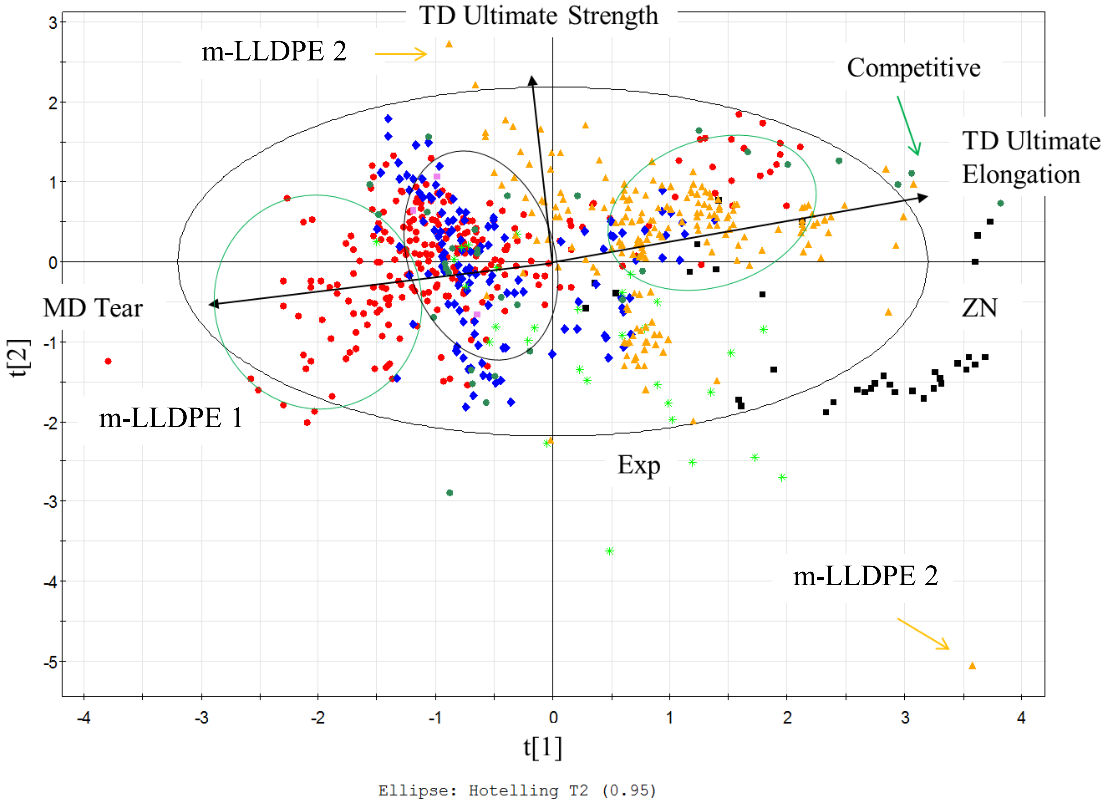
3D PCA plot

Projection onto coordinate planes gives bi-pots, like above.

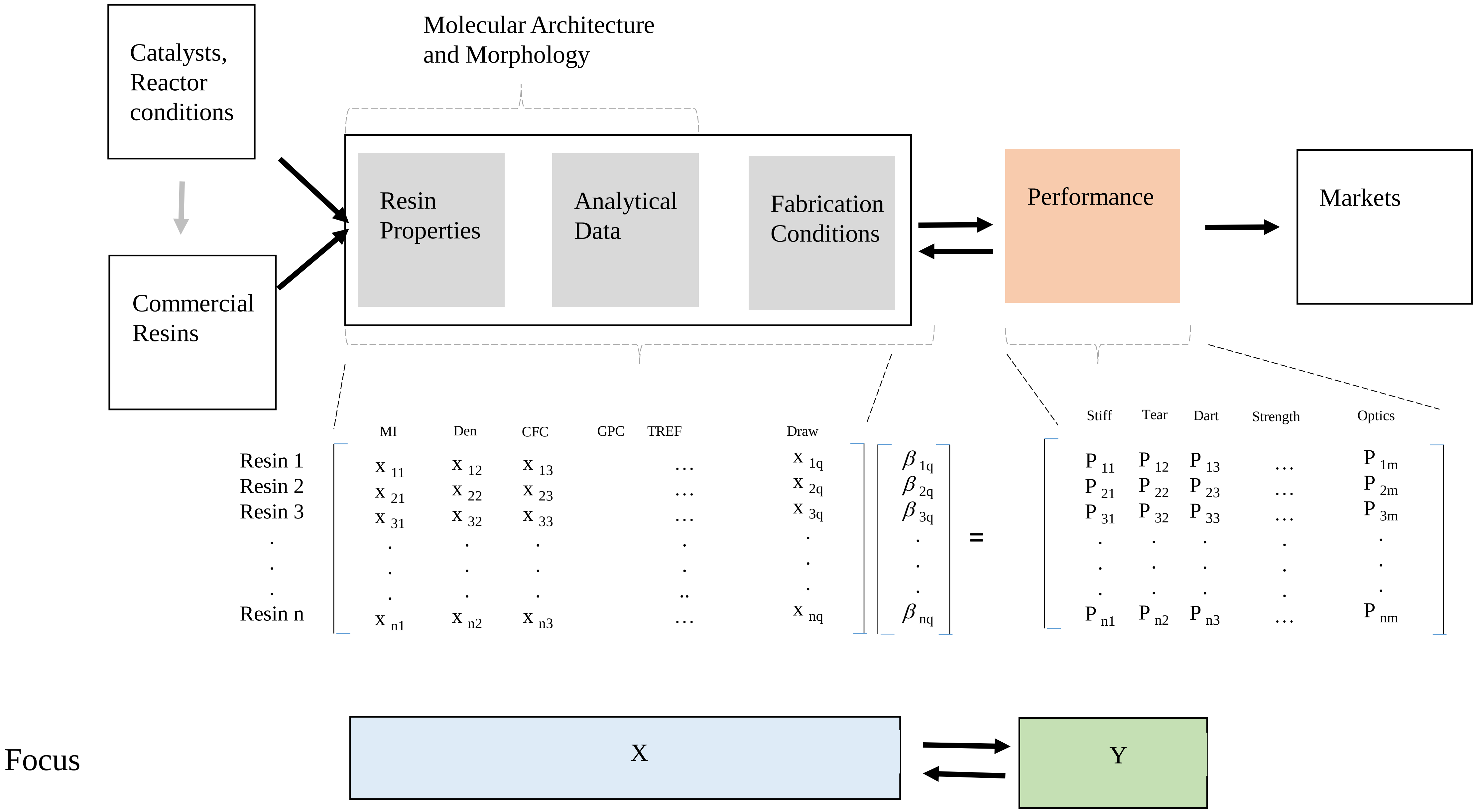
PCA Tear vs. Strength vs. Elongation
T[Comp. 1]/t[Comp. 2]/t[Comp.3]



PCA of MD Tear Resistance and Ultimate TD Performance

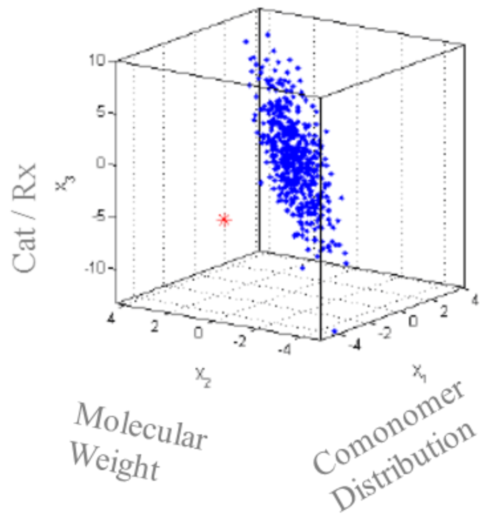


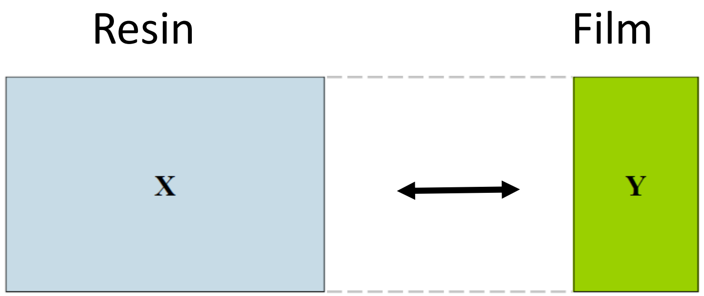
Process Map

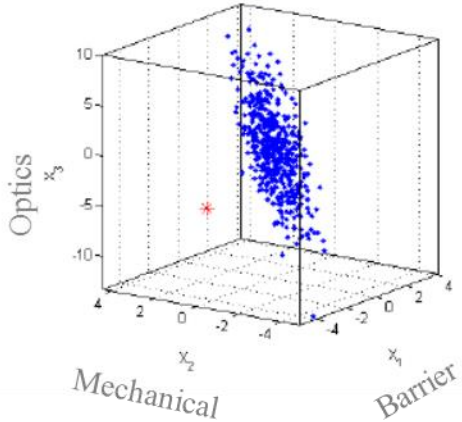


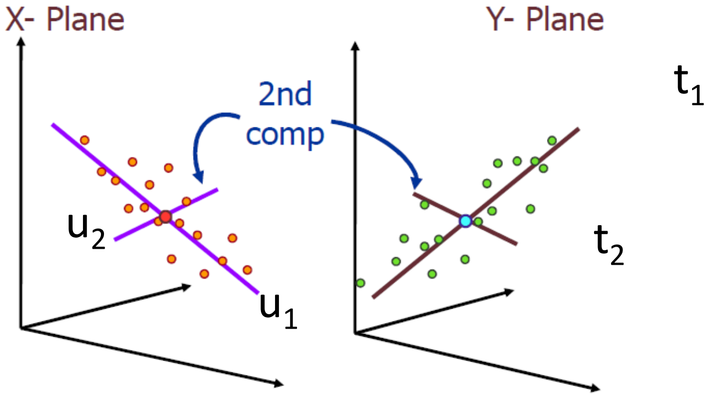
Catalysts, Reactor conditions
Commercial Resins
Molecular Architecture and Morphology
Resin Properties
Analytical Data
Fabrication Conditions
Performance
Markets
MI
Den
CFC
GPC
TREF
Draw
Resin 1
Resin 2
Resin 3
Resin n
x 11 x 12 x 13 … x 1q
x 21 x 22 x 23 … x 2q
x 31 x 32 x 33 … x 3q
x n1 x n2 x n3 … x nq
β 1q
β 2q
β 3q
β nq
=
Stiff
Tear
Dart
Strength
Optics
P 11 P 12 P 13 … P 1m
P 21 P 22 P 23 … P 2m
P 31 P 32 P 33 … P 3m
P n1 P n2 P n3 … P nm
Focus
X
Y

PLS Background

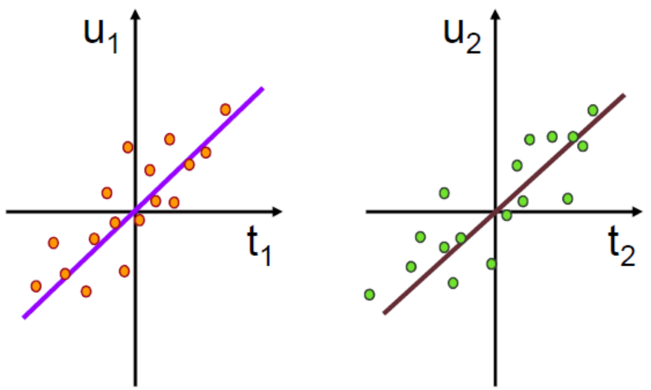




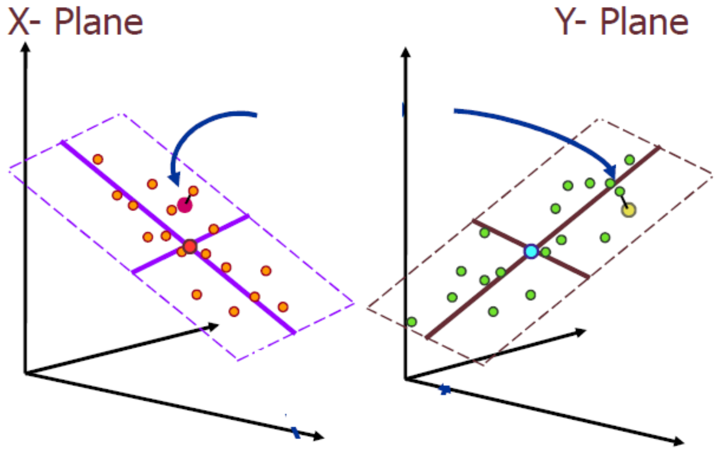




Principal Component Analysis

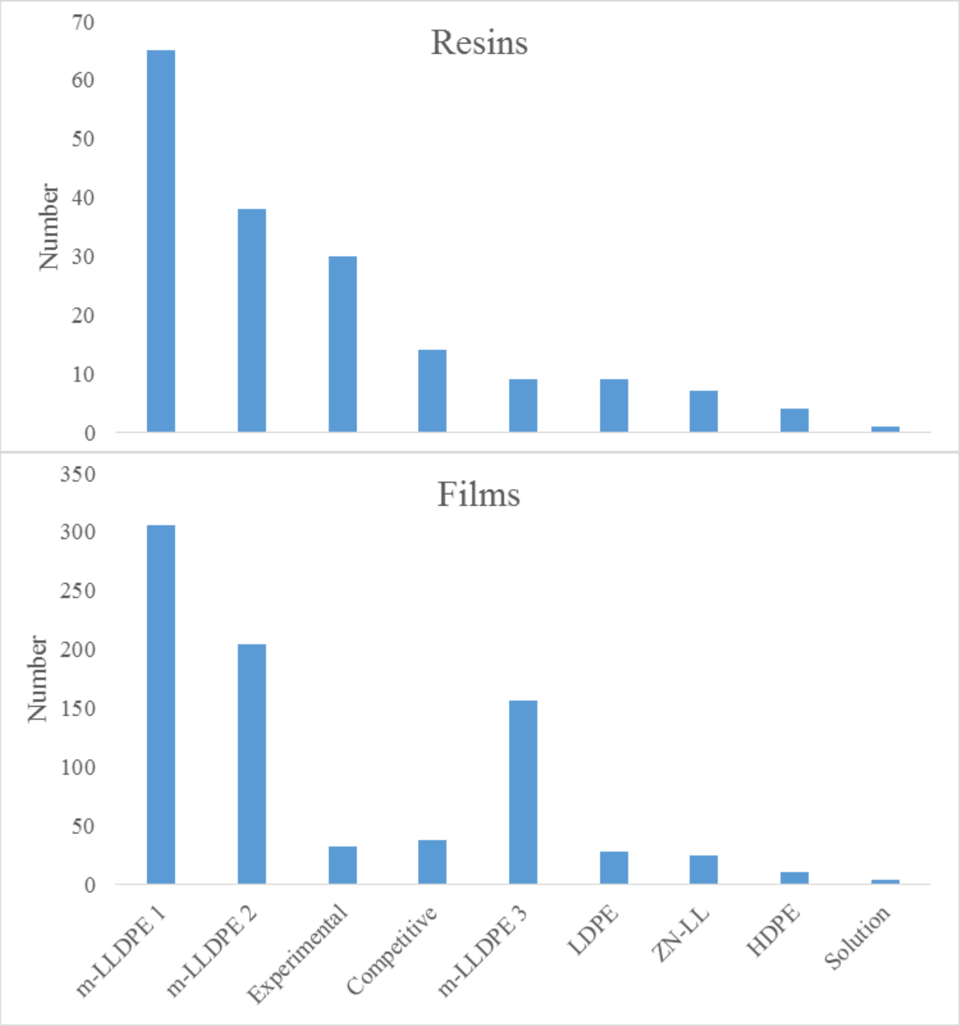


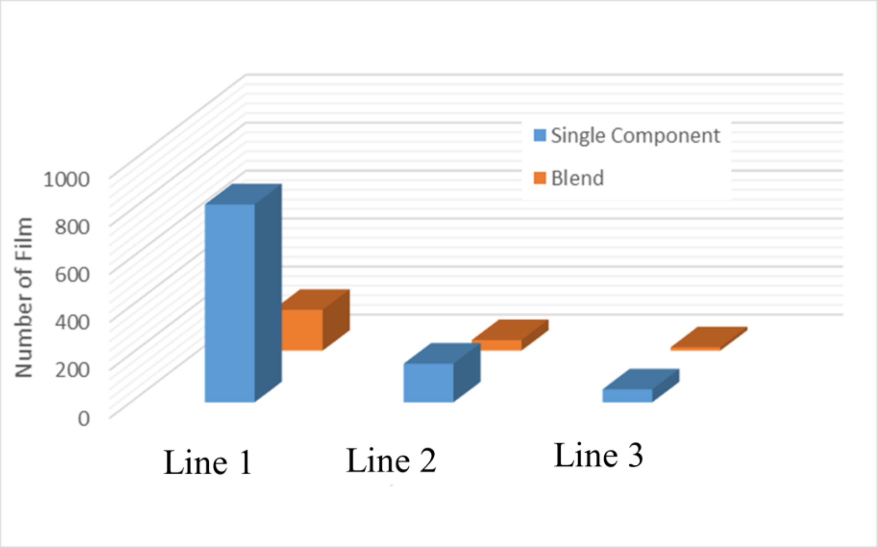
Principal Component Regression



+ 1 K Films by Resins and Line

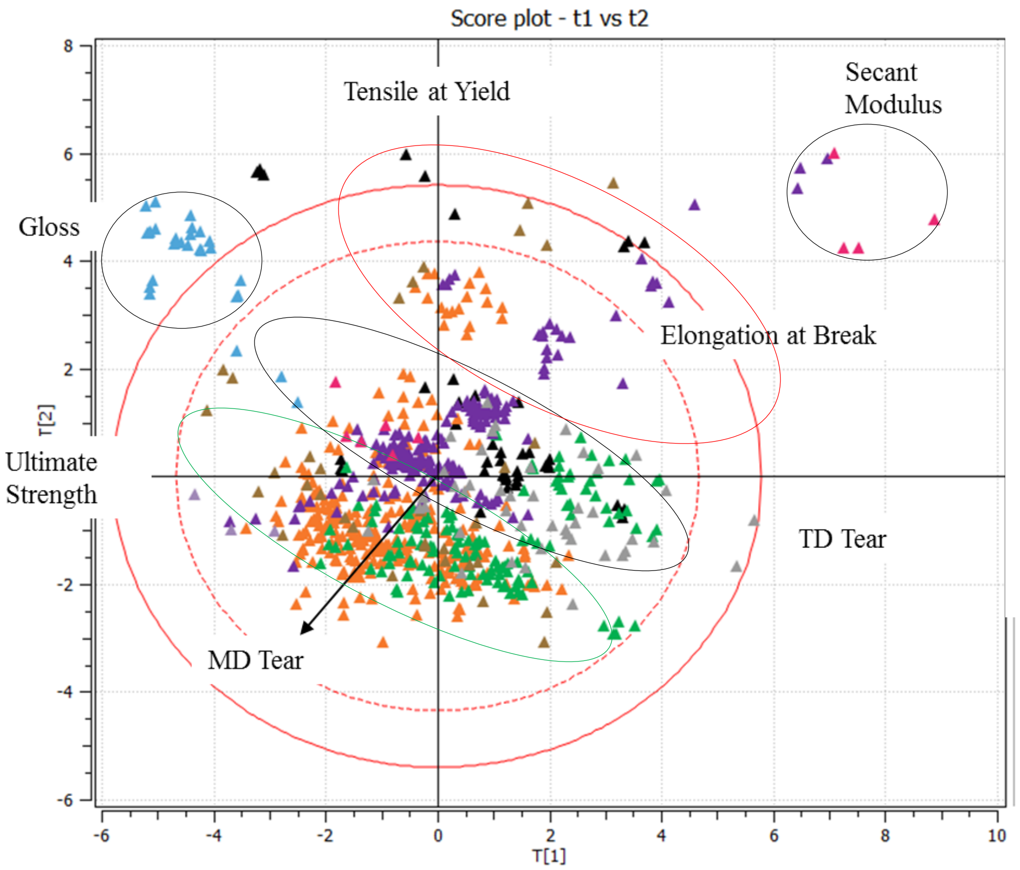
Resin Family	Density (g/cc)	I2 (g/10 min)	I21 (g/10 min)
Competitive	0.906 - 0.941	0.56 - 1.8	14 - 32
m-LLDPE 1	0.904 - 0.933	0.35 - 1.3	8 – 34
m-LLDPE 2	0.894 - 0.957	0.16 - 1.7	9 – 50
m-LLDPE 3	0.903 - 0.928	0.98 - 1.9	15 – 32
Experimental	0.917 – 0.932	0.46 – 1.2	18 - 65
ZN-LL	0.918 - 0.944	0.81 - 3.1	20 – 88
HDPE	0.958 - 0.961	0.45 - 0.7	28 – 32
Solution	0.900	1.2	
HP-LDPE	0.926 – 0.951	0.35 – 2.5	





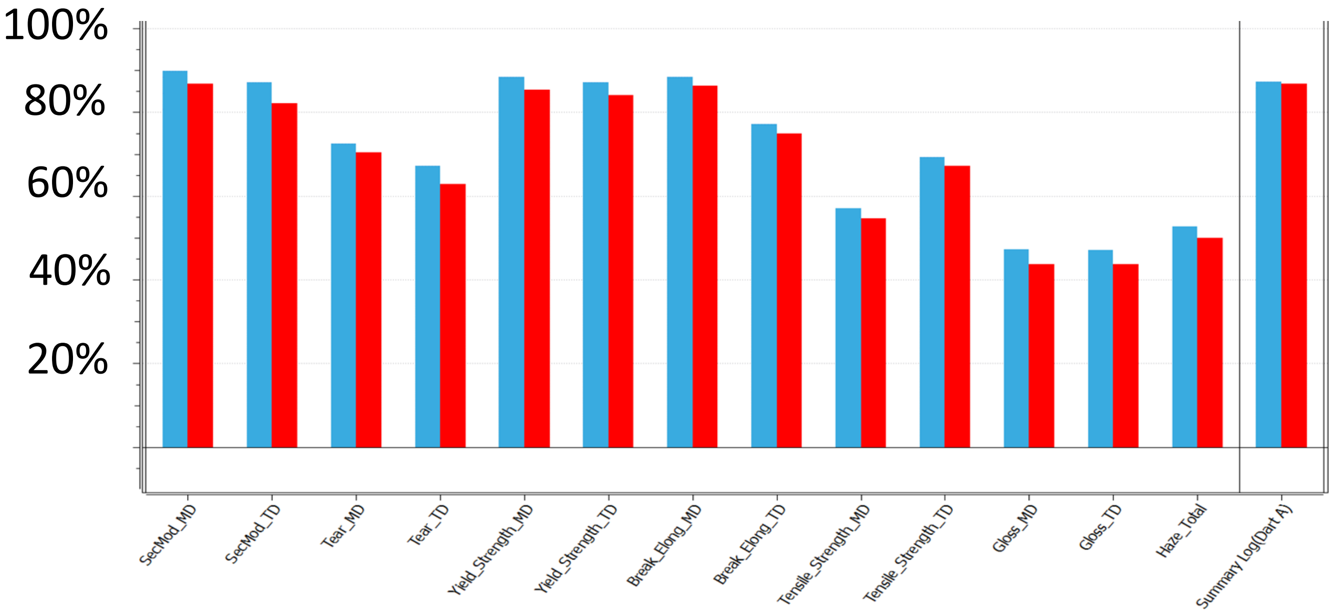
PCA for + 1 K Films

PCA Overlay Plot

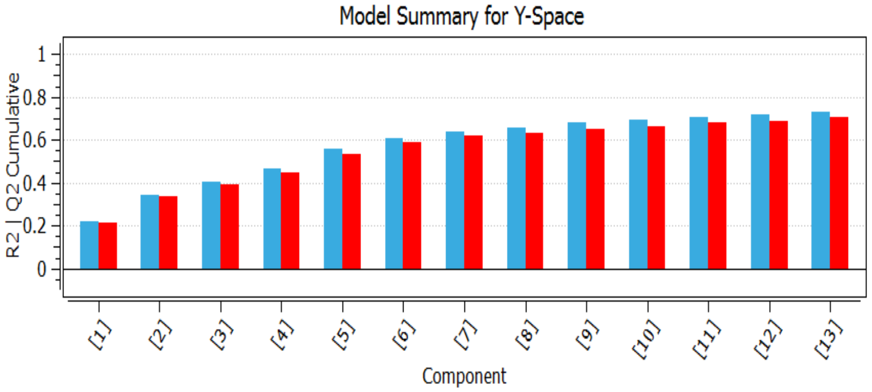


Explains (R^2(cum)) and predicts (Q^2(cum)) > 70% of the variation in the film's balance of properties.

(R^2(cum) and Q^2(cum) by performance variable.



R^2(cum) are shown by blue bars.
Q^2(cum) are shown by red bars, calculated through cross validation



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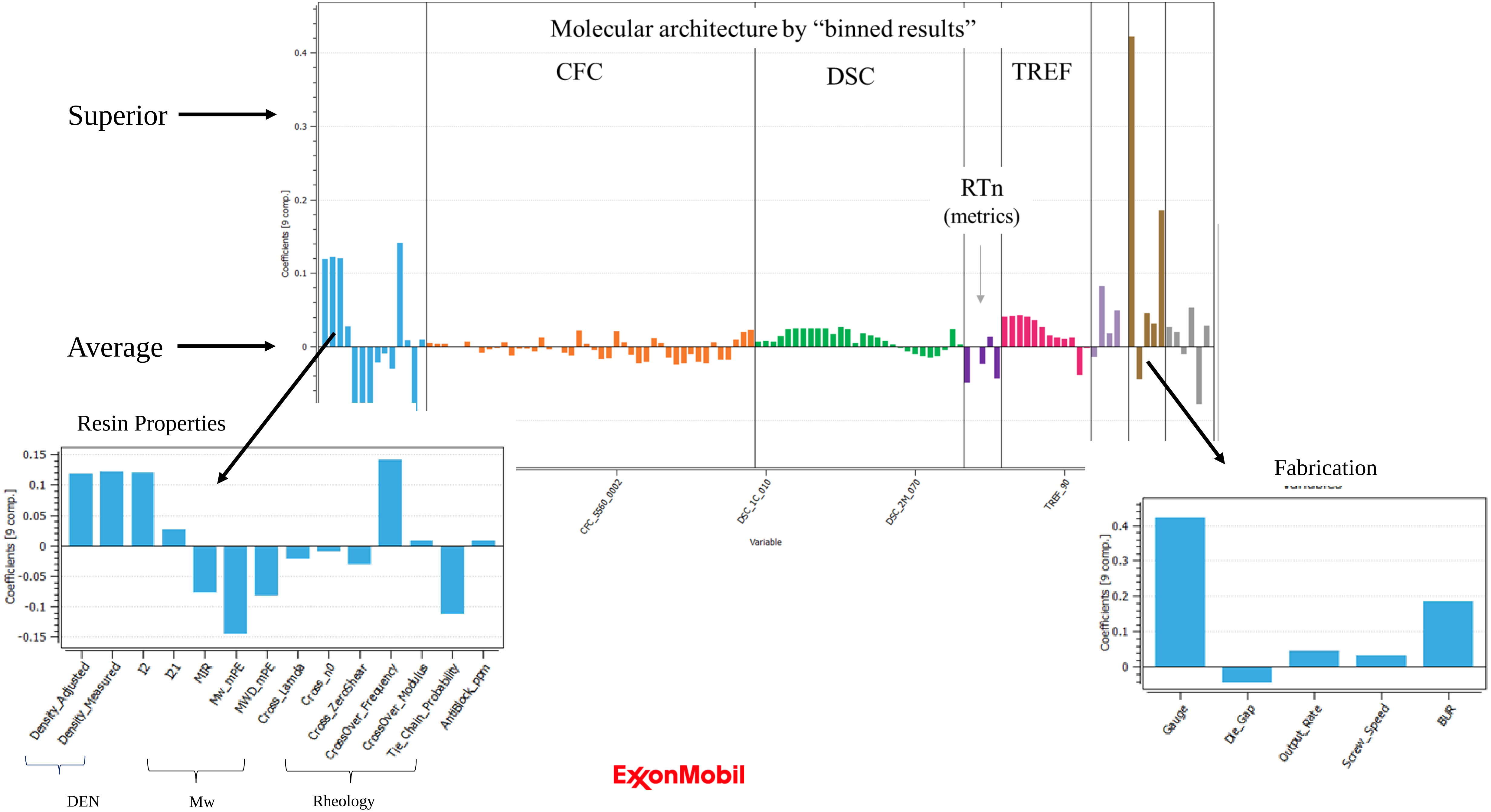
MD Elongation at Break Coefficient Plot



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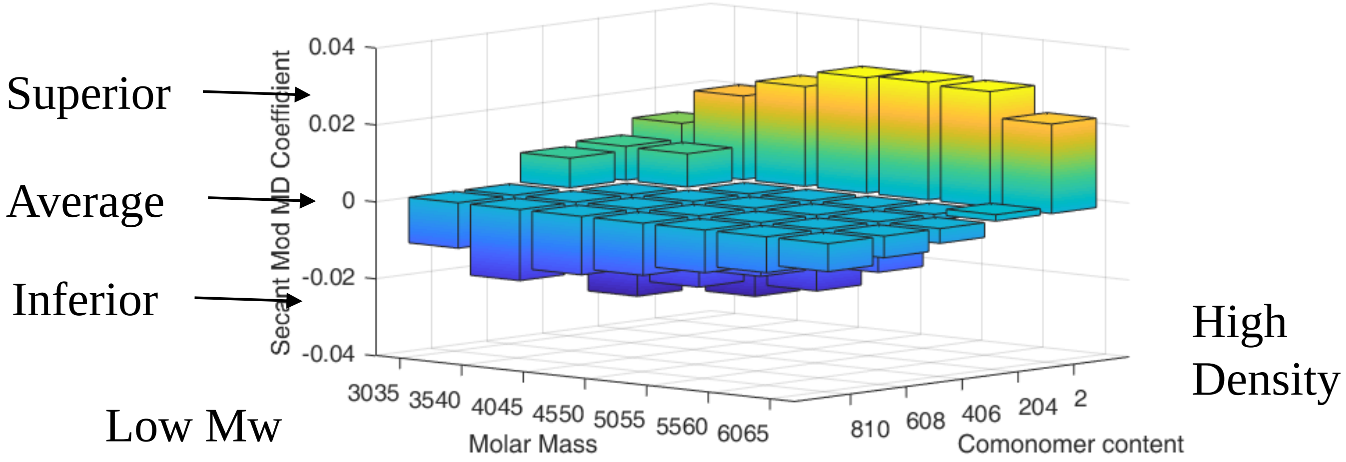
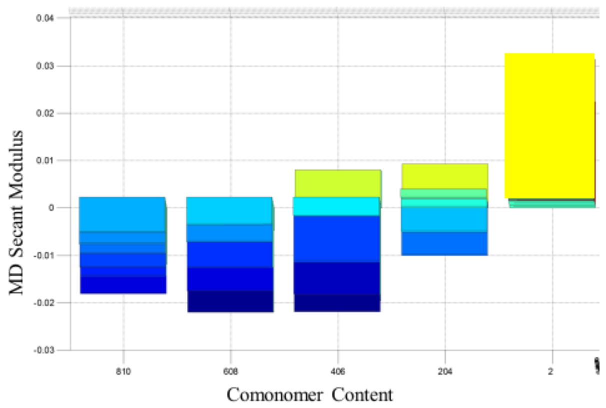
2D Coefficient Plots

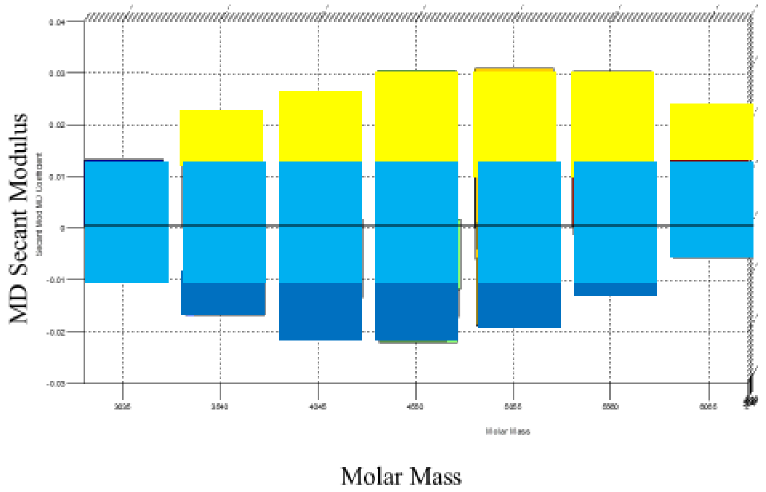
2D Coefficient Bar Graph
MD Secant Modulus vs. Molar Mass and Comonomer Content



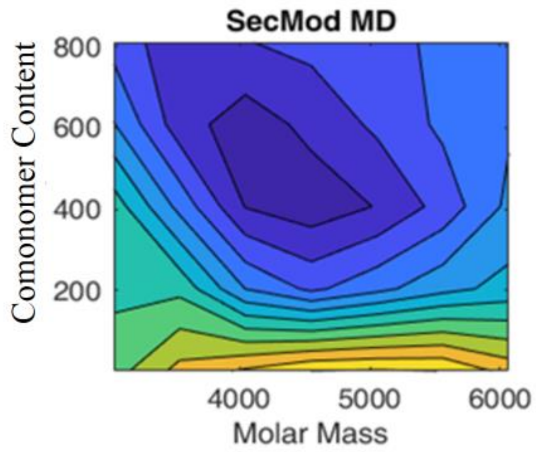
Coefficient Bar Graph
MD Secant Modulus vs. Comonomer Content



Coefficient Bar Graph
MD Secant Modulus vs. Molar Mass

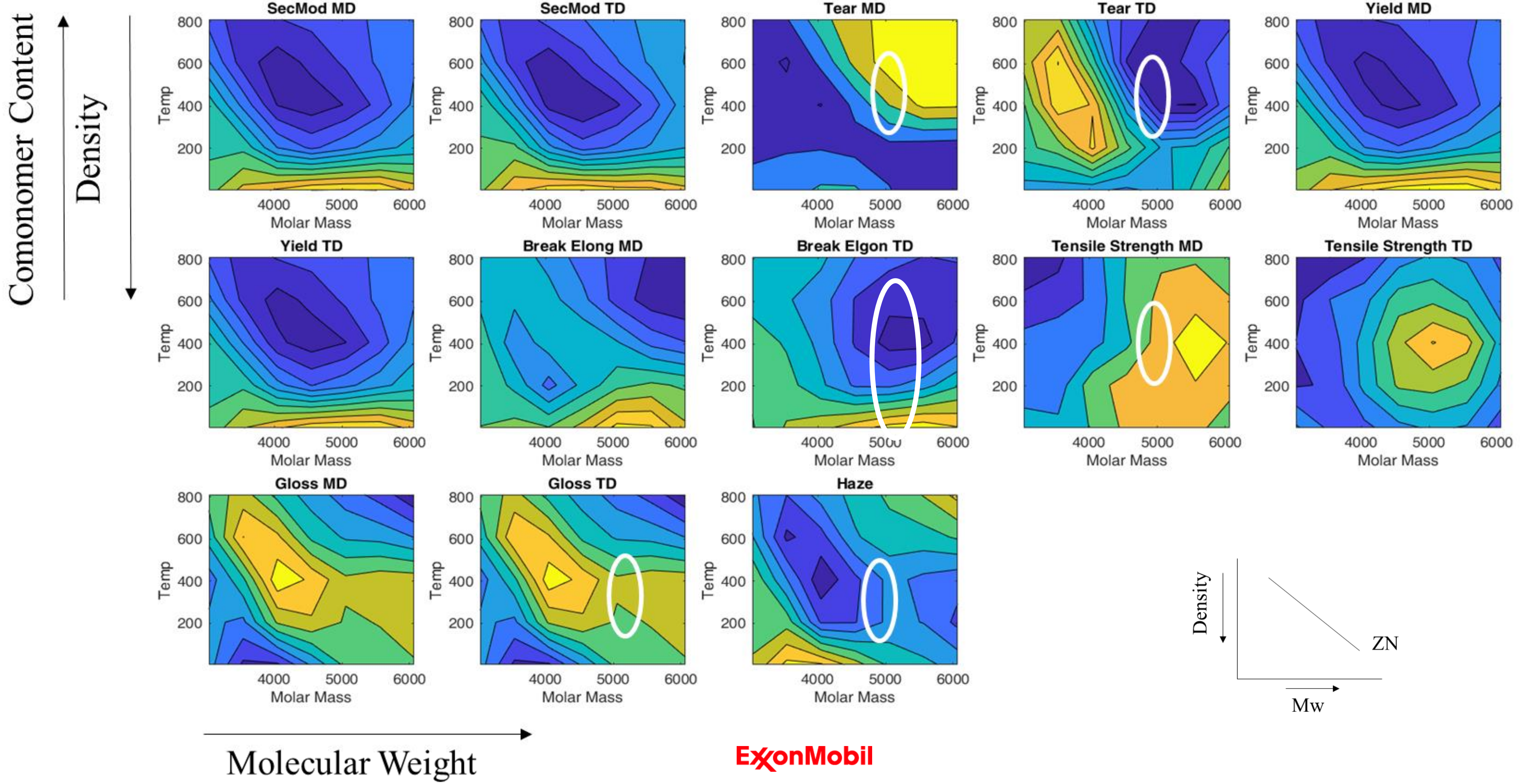


Contour Plot
MD Secant Modulus vs. Molar Mass and Comonomer Content



Coefficient increase with an increase in lighter color and decrease with an increase in darker color.

2D Coefficient Plots



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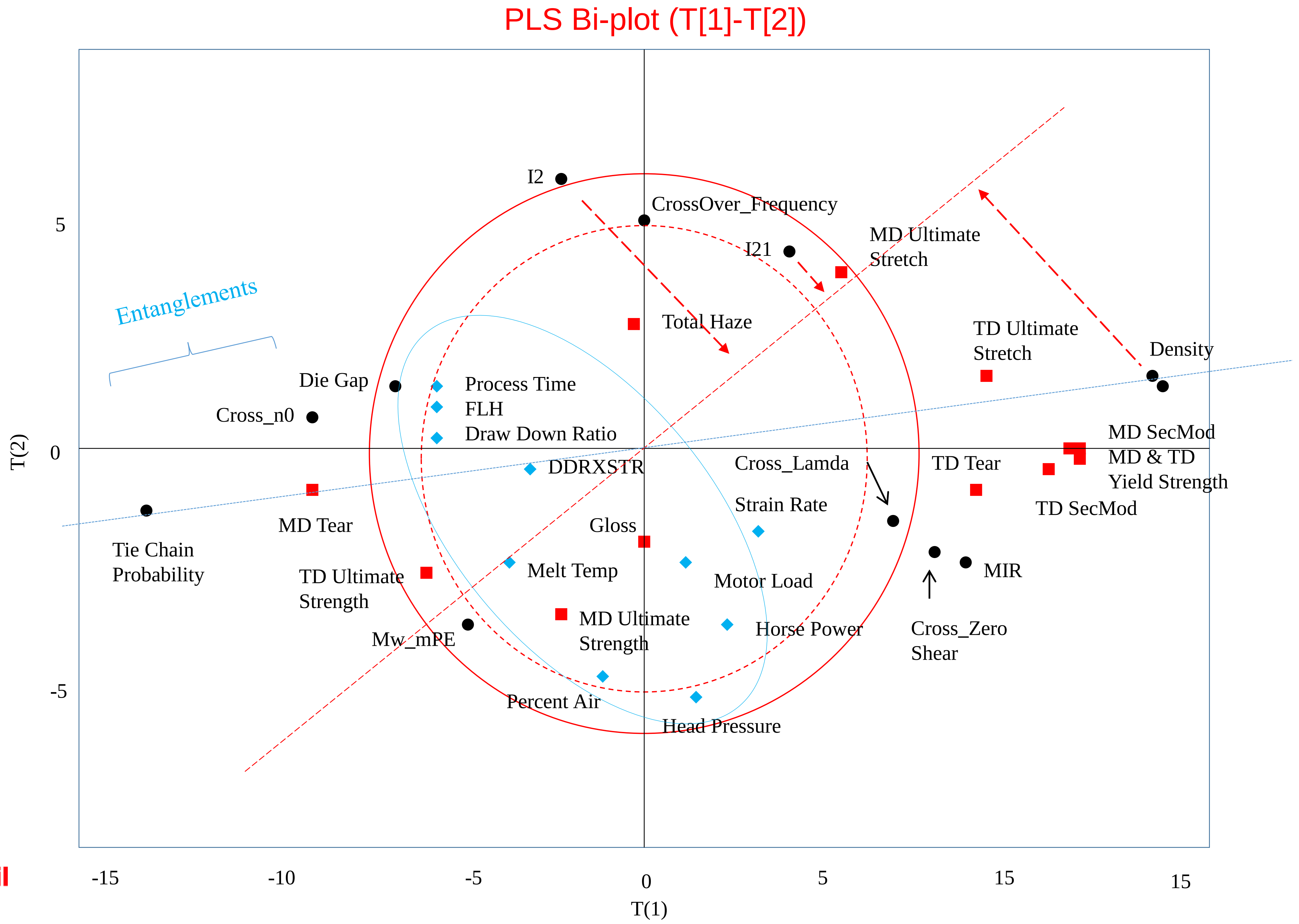
PLS Bi-plot (T[1]-T[2])
Entanglements
I2
CrossOver_Frequency
I21
MD Ultimate Stretch
Total Haze
TD Ultimate Stretch
Density
Die Gap
Cross_n0
Process Time
FLH
Draw Down Ratio
MD SecMod
MD & TD Yield Strength
DDRXSTR
Cross_Lamda
TD Tear
TD SecMod
Strain Rate
MD Tear
Gloss
Tie Chain Probability
Melt Temp
Motor Load
MIR
TD Ultimate Strength
MD Ultimate Strength
Horse Power
Cross_Zero Shear
Mw_mPE
Percent Air
Head Pressure
T(2)
T(1)
5
0
-5
-15
-10
-5
0
5
15
15

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Summary

Film performance depends on resin molecular architecture and film fabrication conditions.

Information on a wide variety of films using a broad spectrum of commercial resins was presented.

Structure-process-property relationships for blown film resins were established using multivariate statistical methods of analysis.

Optimum balance of film properties is obtained for molecular architecture.

Fabrication dependent and independent models show resin molecular architecture affects film performance more than film fabrication conditions.

- Fabrication independent models explain about 50% of the total variation in film performance.
- Fabrication dependent models explain about 70% of the total variation in film performance.
- 20% to 30% of film performance is unexplained by the fabrication dependent model.
- Application to resin blends was shown.

ExxonMobil is using this technology in developing new blown film resins with superior balances of performance.

Disclaimer

Reduce Covariance Matrix into a Diagonal Matrix.

Linear Regression $y = a\,x + b$ Mean Centered $(y - \overline{Y}) = a\,(y - \overline{Y})$ $a = \frac{Cov(x,y)}{Var(x)}$

Extends to multivariate analysis

$$\begin{bmatrix} s_1^2 & s_{12} & s_{13} & \cdots & s_{1m} \\ s_{21} & s_2^2 & s_{23} & \cdots & s_{2m} \\ s_{31} & s_{32} & s_3^2 & \cdots & s_{3m} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ s_{n1} & s_{n2} & s_{n3} & \cdots & s_m^2 \end{bmatrix} \longrightarrow \begin{bmatrix} s_1^2 & & & & & 0 \\ & s_2^2 & & & & \\ & & s_3^2 & & & \\ & & & \cdot & & \\ & 0 & & & \cdot & \\ & & & & \cdot & s_m^2 \end{bmatrix}$$

$$s(x_1, x_2) = \sum (x_1 - \mu_1)(x_2 - \mu_2)/(n-1)$$

S $\longrightarrow$ L

The covariance matrix is symmetric and non-singular. It is reduced using an orthonormal matrix U.

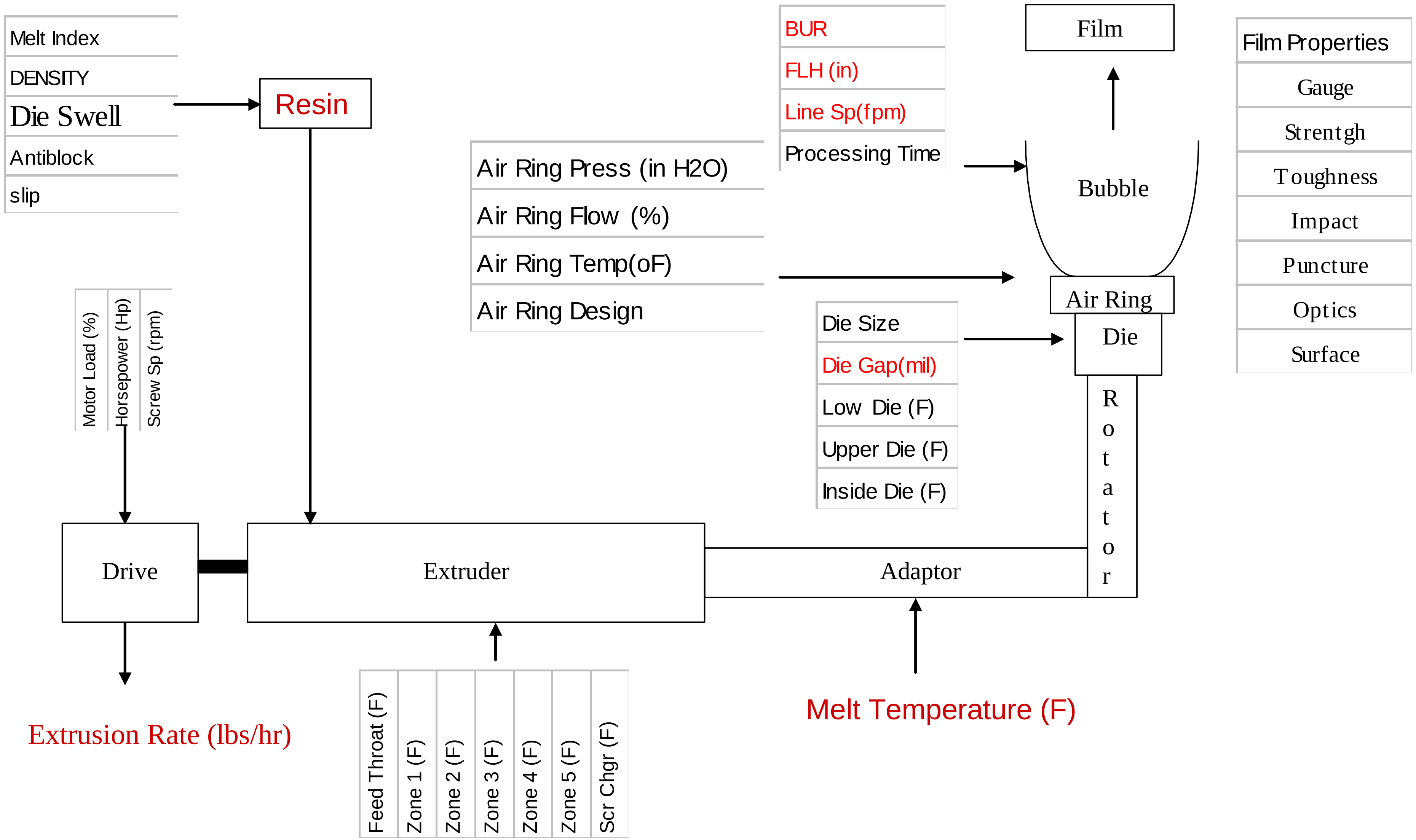
U'SU = L Where the components of U are the Eigen vectors of S, and those of L are the Eigen values of S.

Solve U'SU for the Eigen values of S using the characteristic equation: $|\,S - lI\,| = 0$

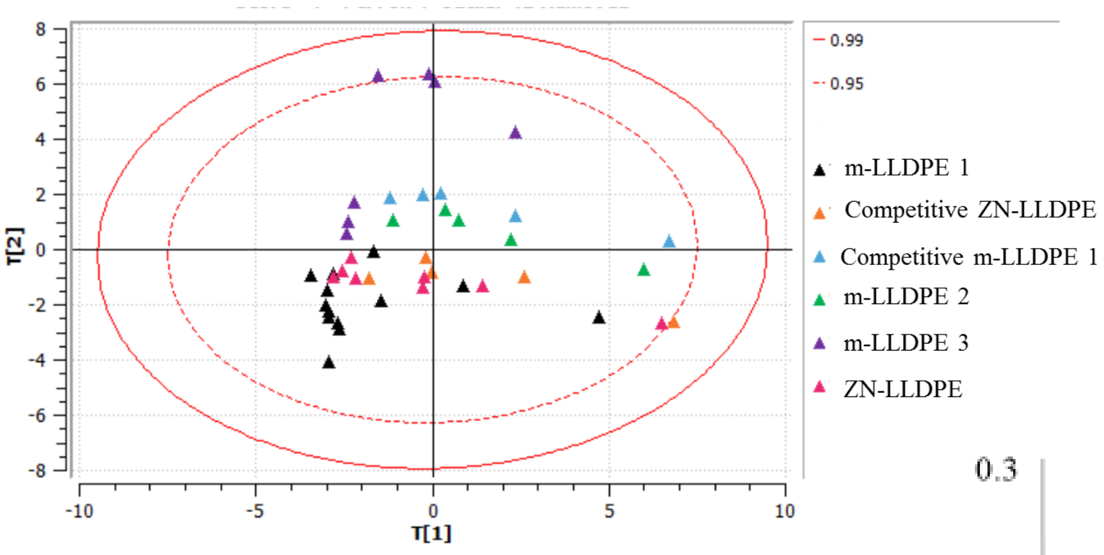
Use the Eigen values (u_i) to determine the Eigen vectors(l_i): $\left[S - lI\right] t_i = 0$

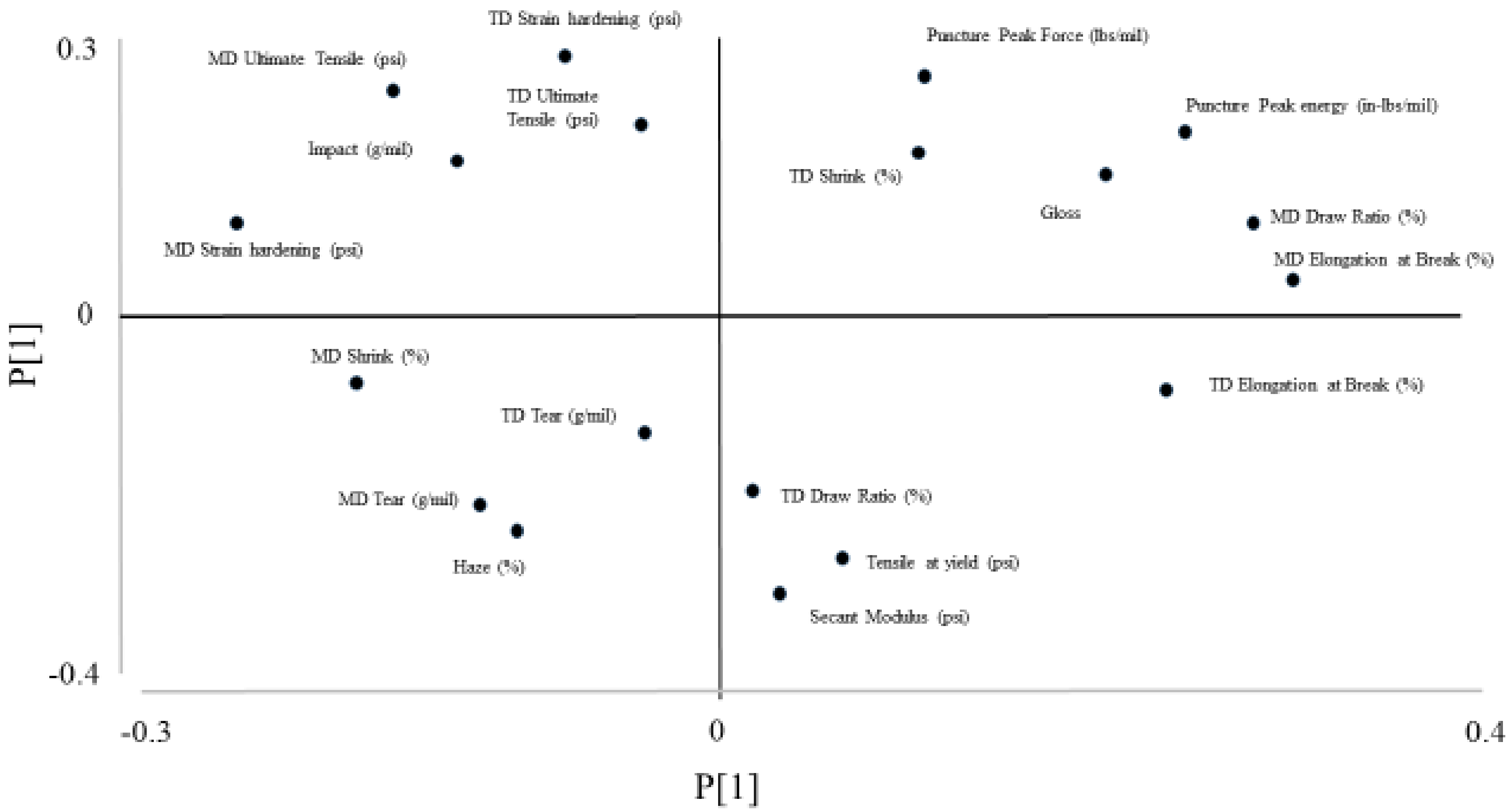
Technically, the Eigen vectors and values are determined iteratively using algorithms like NIPALS.

Blown Film Line Process Map



PCA for a Small Data Set





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Test Methods

Test Description	Method	Based on
1% Secant Modulus	ExxonMobil Procedure	ASTM D882-95a
Tensile Test	ExxonMobil Procedure	ASTM D882-95a
Elmendorf Tear	ASTM D1922-15	
Dart Impact (Method A / B)	ExxonMobil Procedure	ASTM D1709-91
Puncture Test**	ExxonMobil Procedure	ASTM D 5748
Haze	ASTM D1003-13	
Gloss	ASTM D618	ASTM D2457-90
Average Gauge Mic*	ExxonMobil Procedure	ASTM D374
Resin Density	ASTM D1505-10	
Melt Index	ASTM D1238-13	
CFC Test	EM314-R4	
SAOS (Shear Rheology)	EM513-R2	
Rheotense (Extensional Rheology)	RHE04-3.3 & EM 514-R1	
TEM (General TEM Analysis)	EM-116 R2	

*Calibrated yearly.

**A steal probe is used instead of a Teflon coated probe.

DSC Analysis:

Samples of resin or film (3-5 mg) sealed in aluminum sample pans were heated and cooled in differential scanning calorimetry (DSC) at 10 °C/minute from -60 C to +220 C, from +220 C to -60 C and again from -60 C to +220 C with no hold time between each heating and cooling step. Each sample's heat of fusion (ΔH_f) was determined from its total heat flow (ΔH in J/g). Melting temperature was measured and reported during the second heating cycle (or second melt). Each sample's degrees of crystallinity was determined from its thermogram using the enthalpy of fusion of a perfect polyethylene crystal (ΔH_f^o) of 4110 J/mole. Common heats of fusion (ΔH_f^o) reported in the literature for a pure crystalline polyethylene ranges from 3977 J/mole to 4032 J/mole. The cumulative heat of fusion of each polyethylene was determined and the temperatures at 50%, 60%, 70% and 80% of the maximum cumulative heat of fusion noted.

General References on Analytical Methods

Cross explains linear rheology

$$\eta_\gamma = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + k\gamma^n}$$

η_0 is zero shear viscosity
k is a related to the relaxation time of the polymer in solution
γ is shear rate
n is the power law flow index

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GPC explains linear rheology using Double Reptation Theory

$$G'(\omega) = 2G_{No} \times \sum_{i=0}^{N} w_i \times \sum_{j=i}^{N} w_j \times \frac{Z_i^2}{1+Z_i^2}$$

$$G''(\omega) = 2G_{No} \times \sum_{i=0}^{N} w_i \times \sum_{j=i}^{N} w_j \times \frac{Z_i}{1+Z_i^2}$$

$$Z_i = \omega\tau_e (M_i/M_e)^{3.4}$$

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