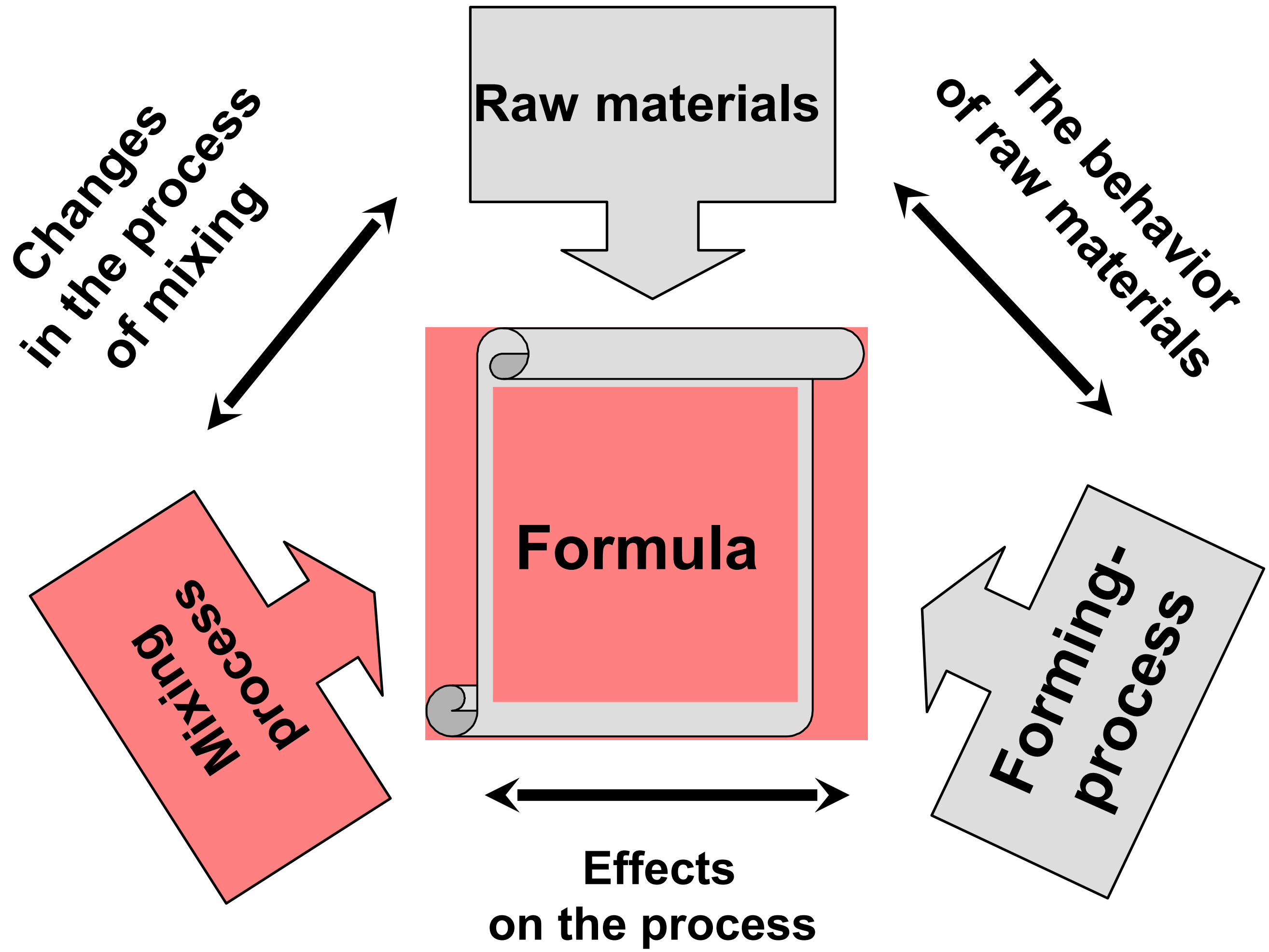
EUROPE Rubber Industry FORUM - 2017
All about rubber compounding

HJG

Review of Rubber Mixing
&
Effect on Polymer / Compound Performance

ERIF 2017
Vienna: 10. – 11. May

RIDT
Rubber Industry
Department @ TechnoBiz


Raw materials
Changes in the process of mixing
The behavior of raw materials
Formula
Mixing process
Forming-process
Effects on the process

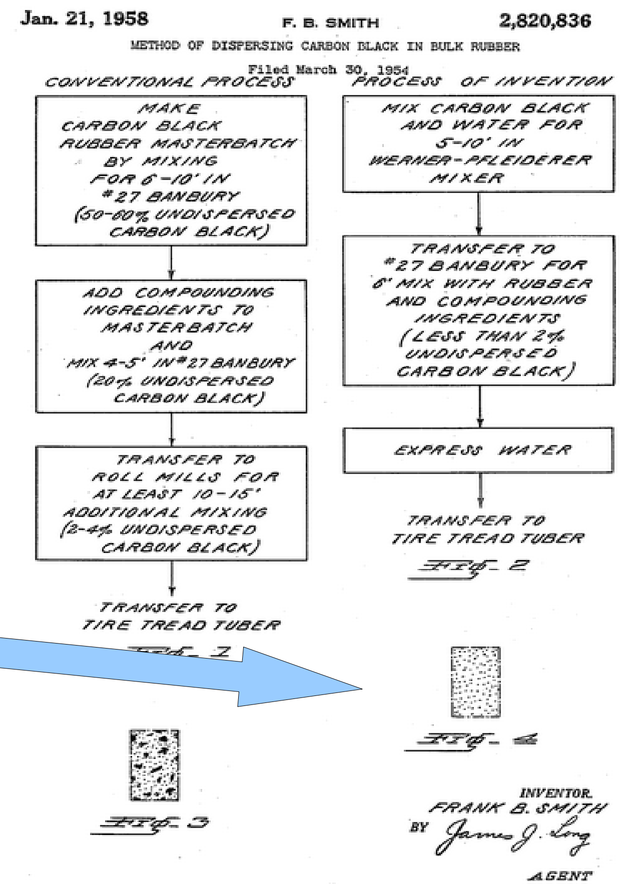
- **Mixing gives reason to changes of ingredients and of reactions between the ingredients**
  - **Mixer behaves like a reactor**
  - **In addition to mechanical work on distribution and dispersion**
- **Polymer Changes**
  - **MW, MWD and LCB**
  - **Radical reactions of polymer with Carbon Black**
- **Protection / Processing Aids**
  - **Ingredients with functional groups reacting with polymer**
  - **Acid / Base Reactions**

Mixing

What is the goal of Mixing?

- **Compound, which can be processed in the desired machines, turned into a part, which meets customer expectations**
  - **Viscosity of compound – processing**
  - **Dispersion of Filler – physical properties**
  - **Homogeneity**
  - **Rheology – Cure kinetic**

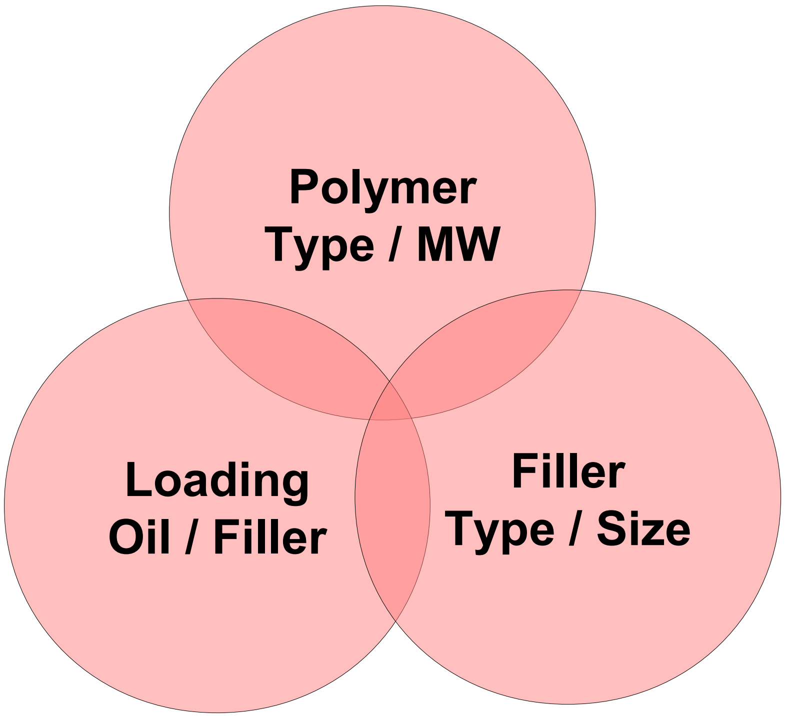
US 2820836 A



Mixing

What is the conflict in Mixing?

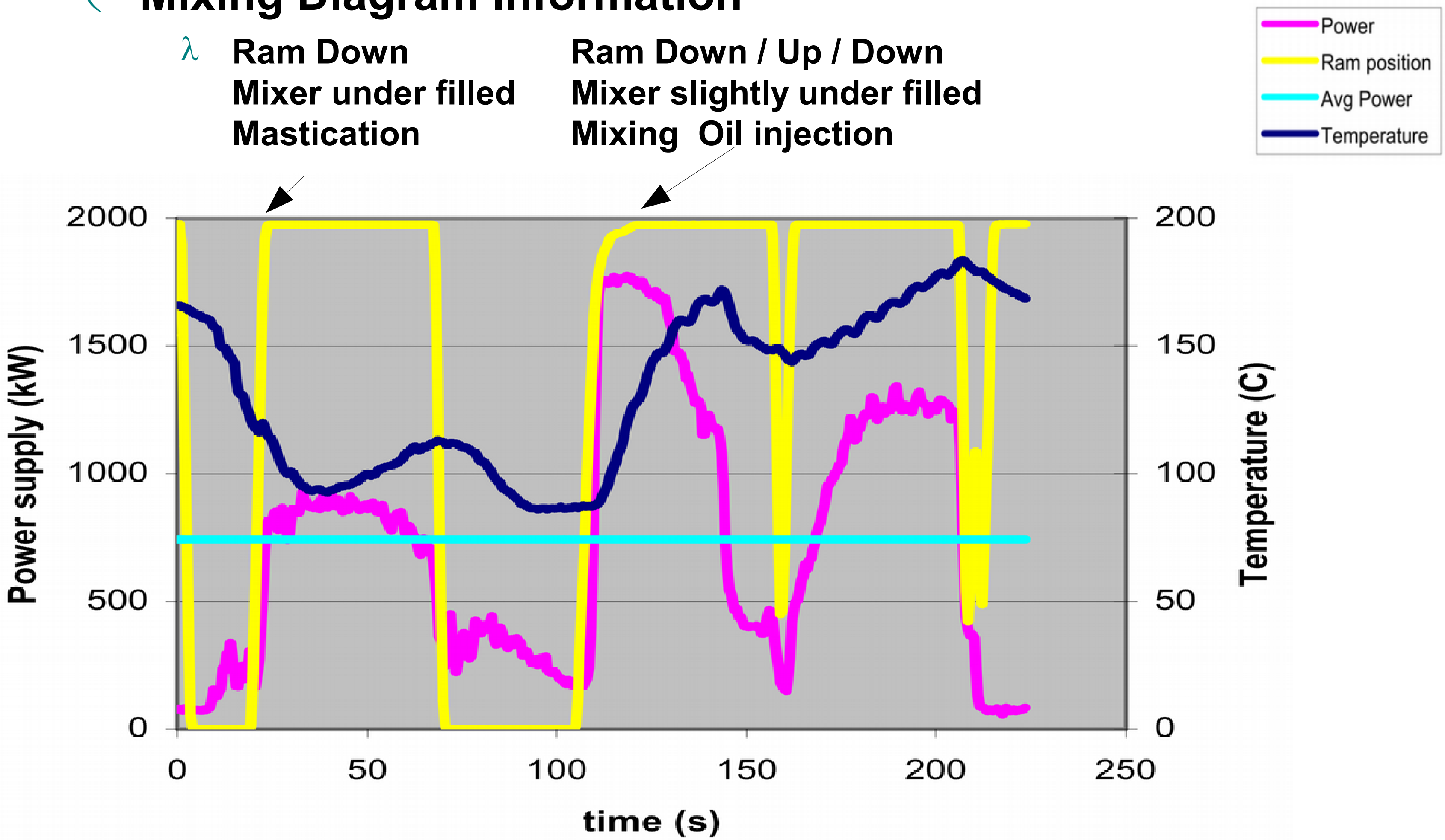
- **Viscosity of compound:**
  - **Viscosity correlates to MW: Performance – Higher is better Processing –**
    - **Lower is better: IM**
    - **Higher is better: CM, Extrusion**
- **Dispersion of Fillers**
  - **Temperature rise through high shear correlates to:**
    - **MW (+ Type of Polymer), Filler (Type) / Oil loading**
- **Rheology – Cure kinetic**



Source: Nijmann Vredestein

Mixing Diagram Information

- **Ram Down** / **Mixer under filled** / **Mastication**
- **Ram Down / Up / Down** / **Mixer slightly under filled** / **Mixing Oil injection**



Source: Thesis Ebell

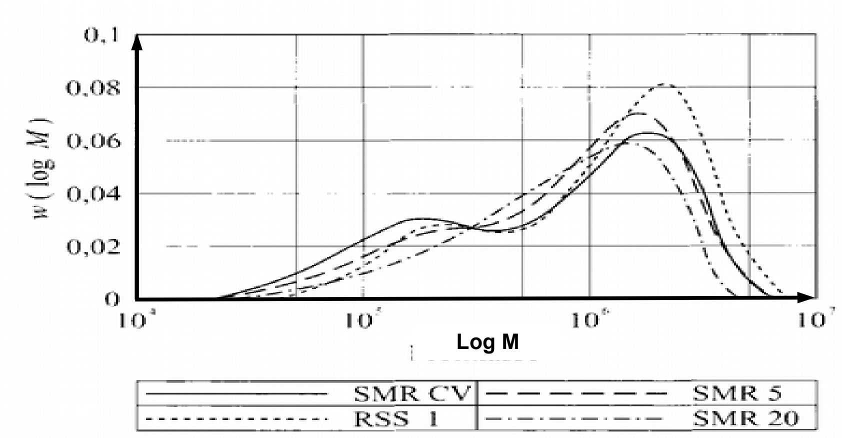
Process factors in order of importance

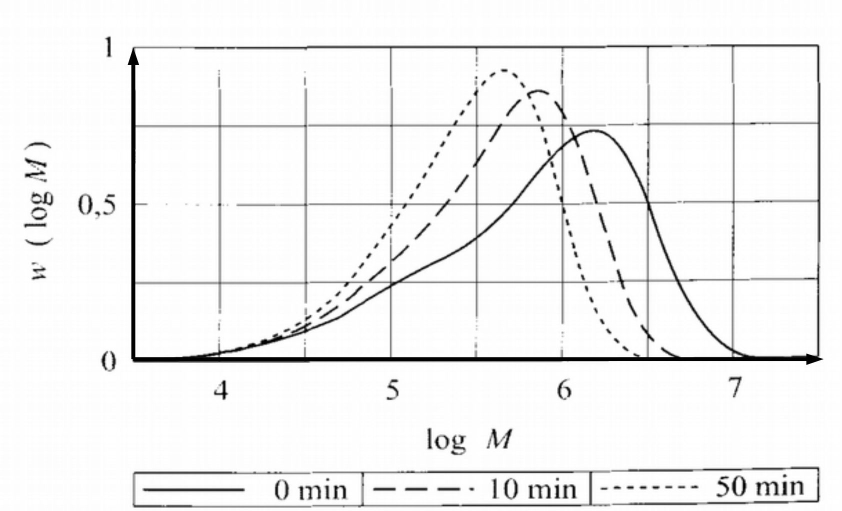
- **Mixing Time or Mixing Unit Work**
- **Rotor Speed**
- **Mixer Temperature**
- **Ram Pressure**
- **Fill Factor (not independent from Ram Pressure)**

Source: Sommer, R Handbook

Mixing / molecular weight change

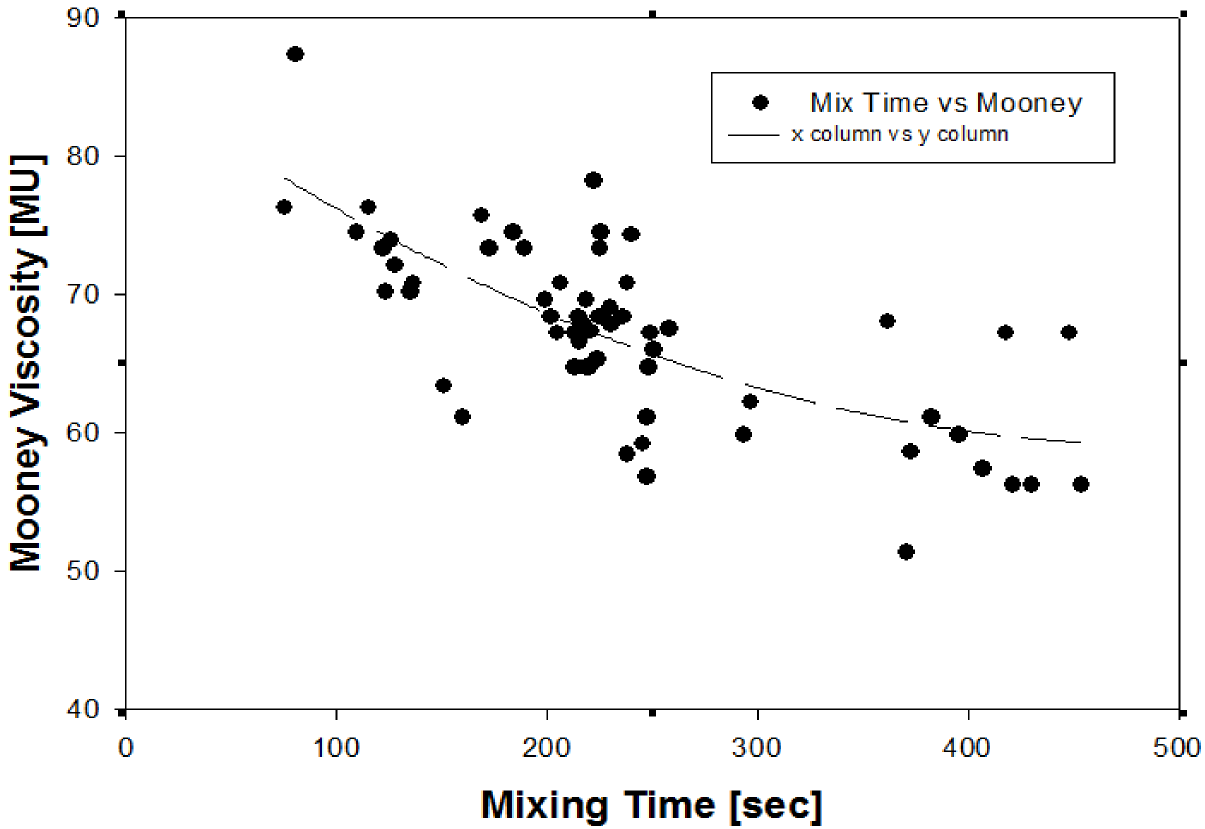
- MW of different NR-Types coagulated and stabilized
  - Bimodal MW distribution
  - MWD of 5 - 10
- Mastication on Mill of SMR 20
  - MW decreases
  - Bimodal MW distribution becomes a broad MW





Source: Thesis Ebell

Mixing of SBR: Mooney Viscosity over Mixing Time *)

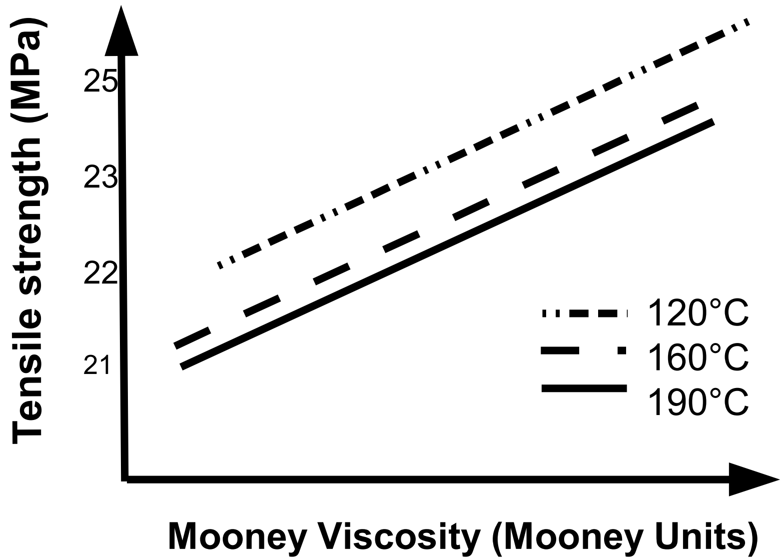


*) other factors neglected

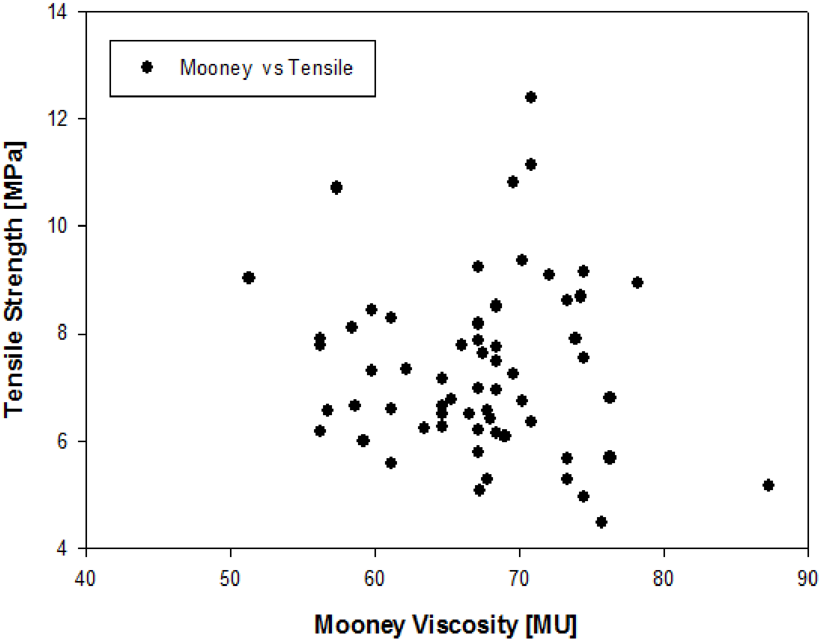
Source: Martin, RCT 1955
Fig left: Thesis Ebell

Mixing of SBR:

Dependence of physical properties on Mooney viscosity of masticated SBR rubber and on temperature of mastication.

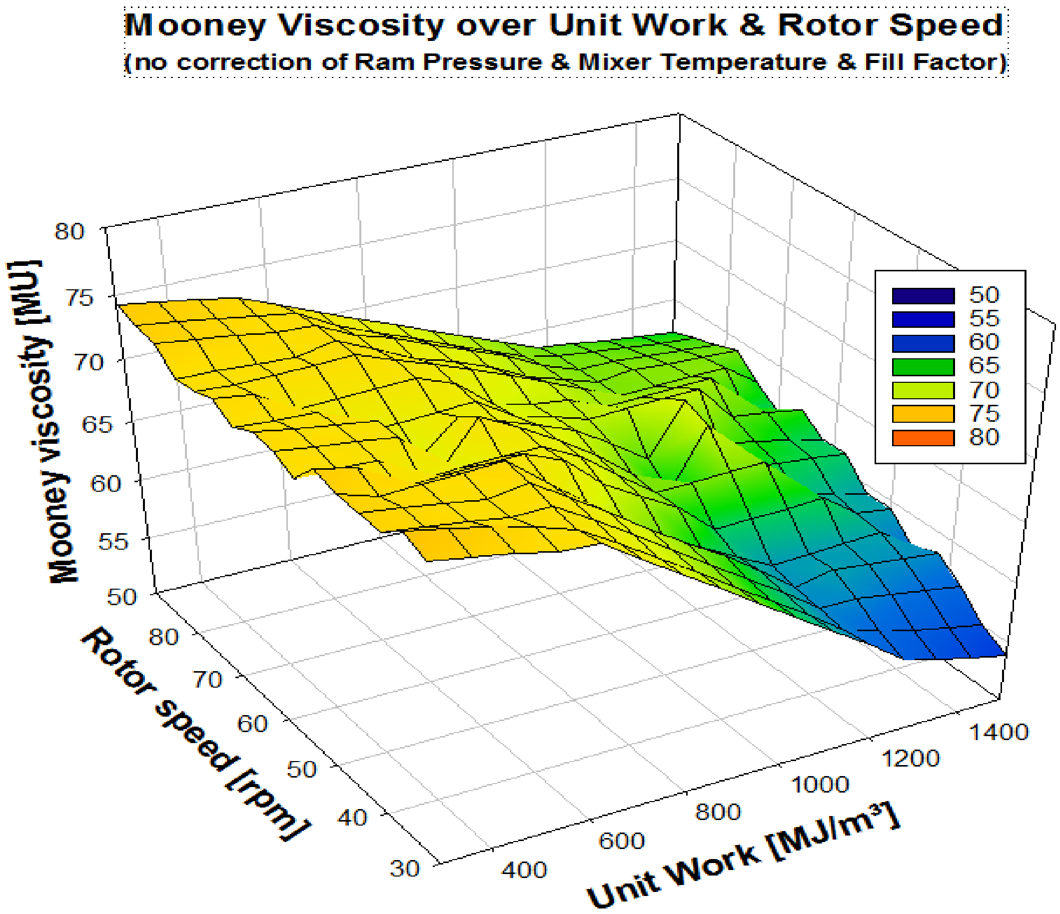


Correlation of Mooney Viscosity with Tensile Strength
(obtained from 5 Factor Mixing Design)



Source: Ebel, Thesis

Mixing of SBR:

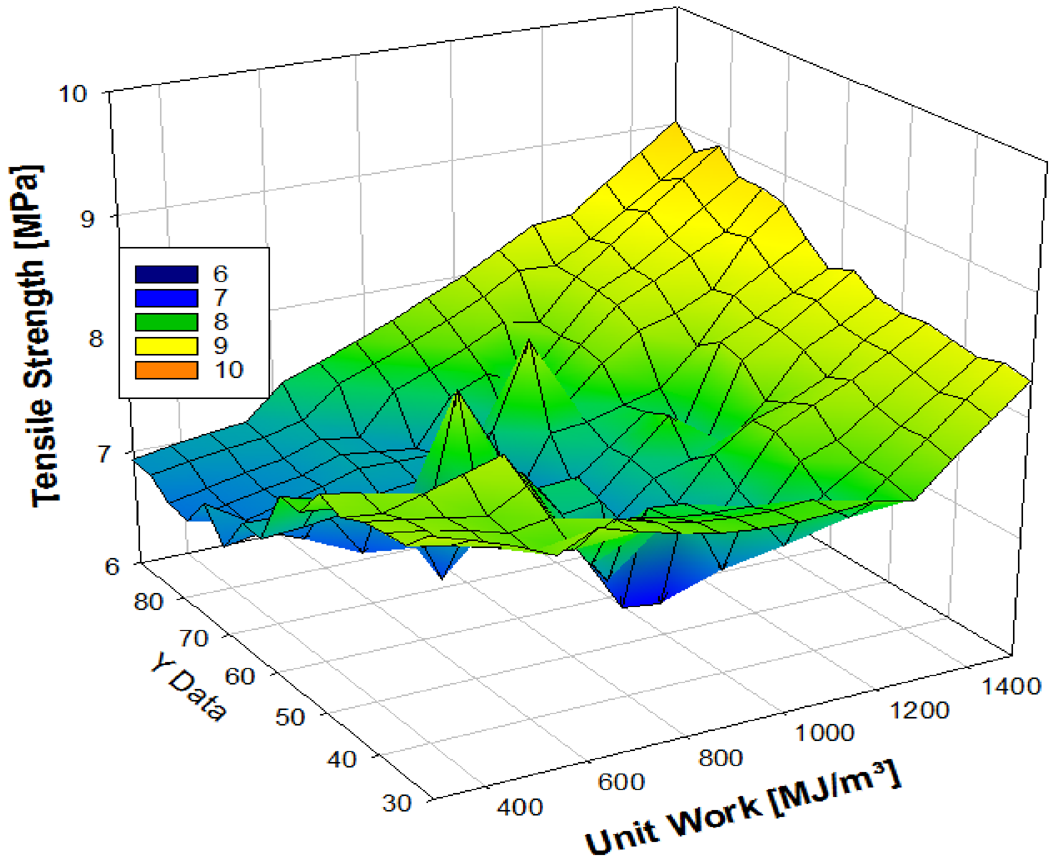


Source: Ebel, Thesis

Mixing of SBR:

Tensile Strength over Unit Work & Rotor Speed

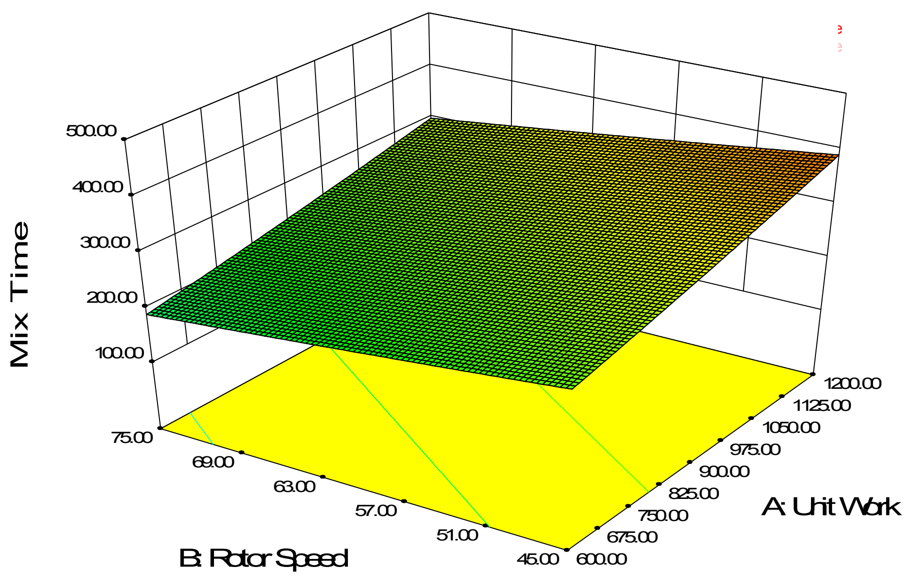
(no correction of Ram Pressure & Mixer Temperature & Fill Factor)

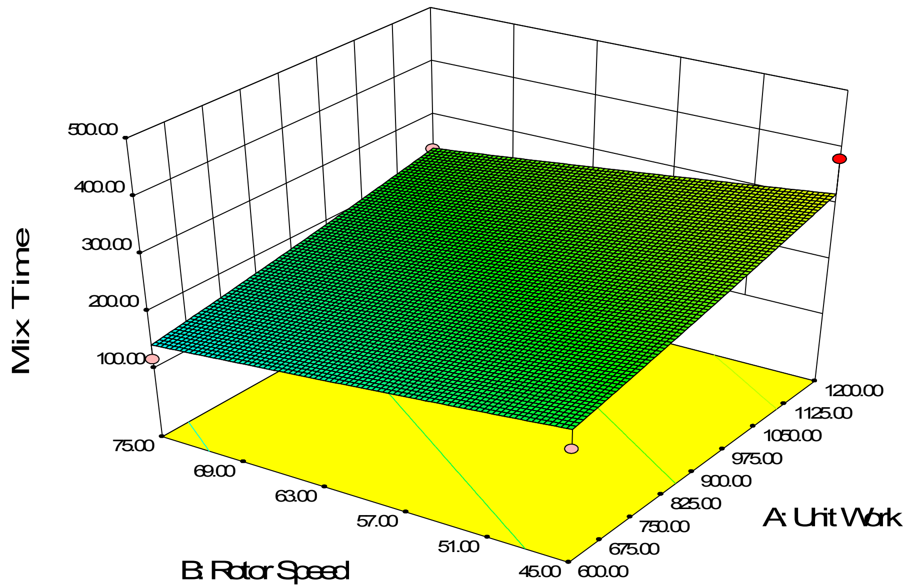


Source: Ebel, Thesis

Mixing of SBR:

- Mix Time over Unit Work & Rotor Speed
- Ram pressure 0.22 (left) - 0.80 (right)

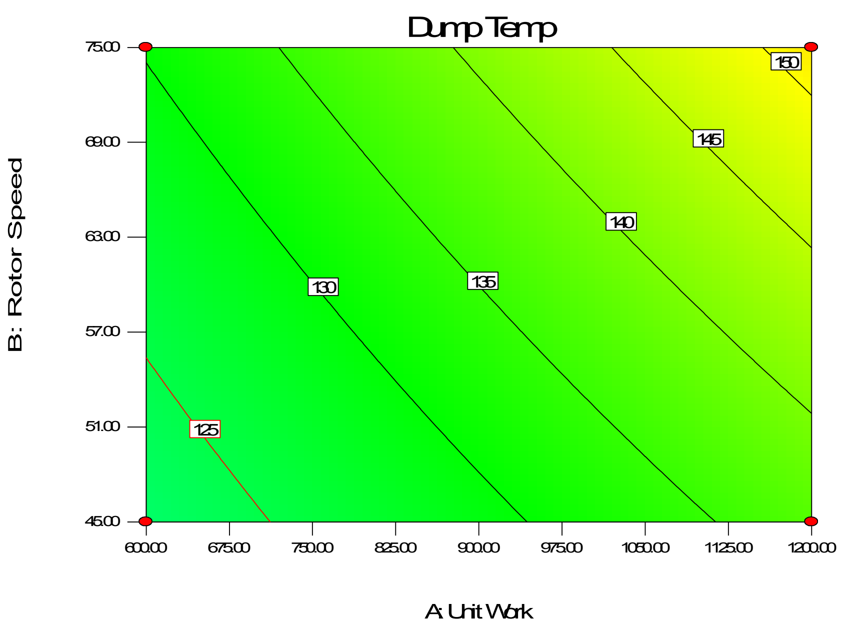


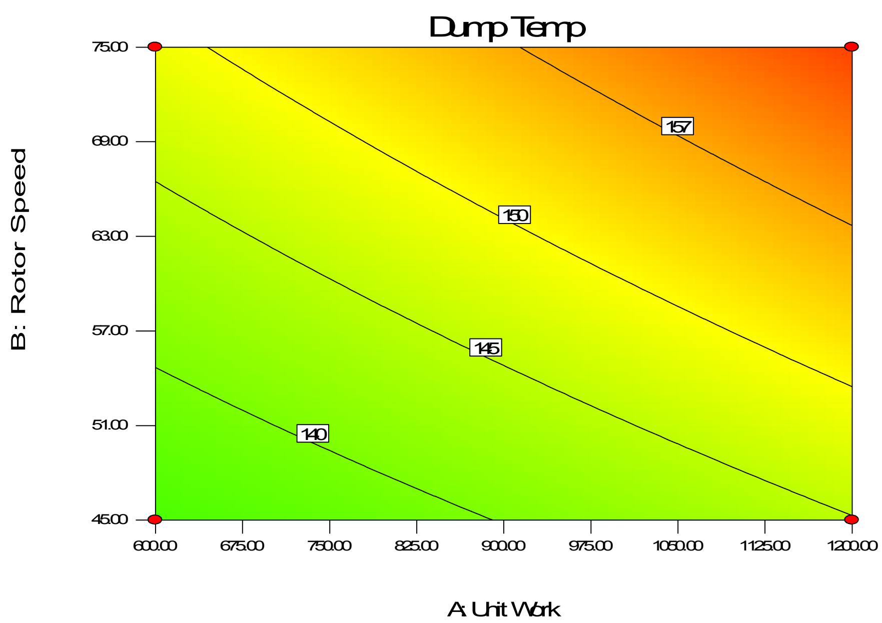


Source: Ebel, Thesis

Mixing of SBR:

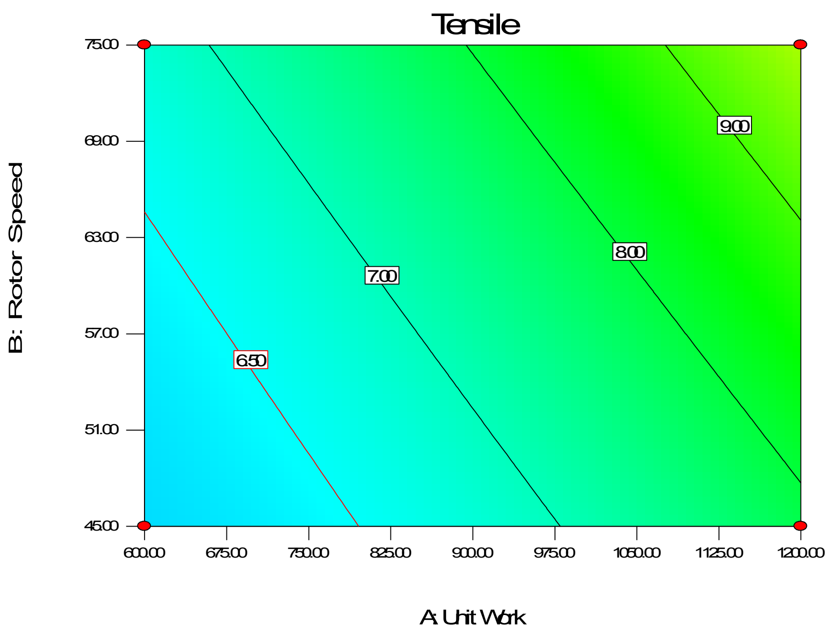
- Dump Temperature over Unit Work & Rotor Speed
- Ram pressure 0.22 (left) - 0.80 (right)

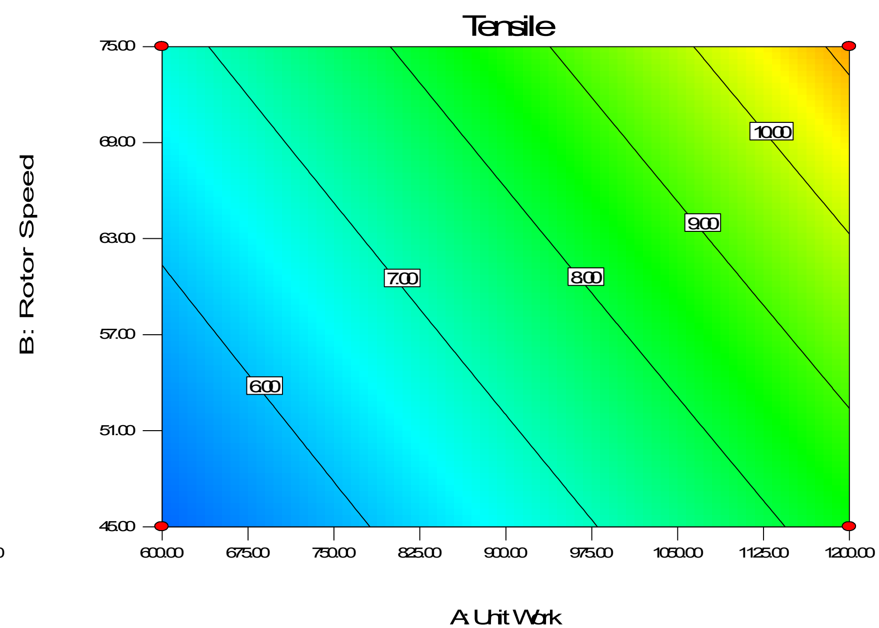




Mixing of SBR:

- **Tensile over Unit Work & Rotor Speed**
- **Ram pressure 0.22 (left) - 0.80 (right)**

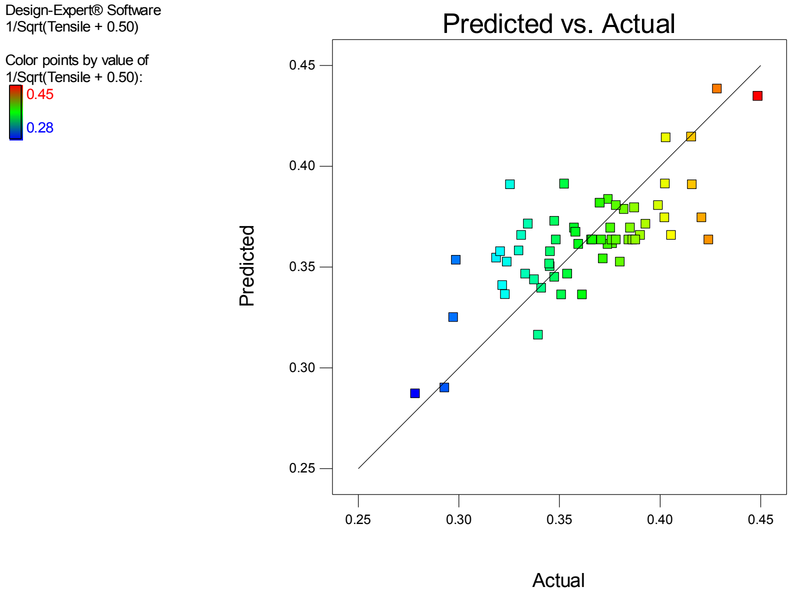


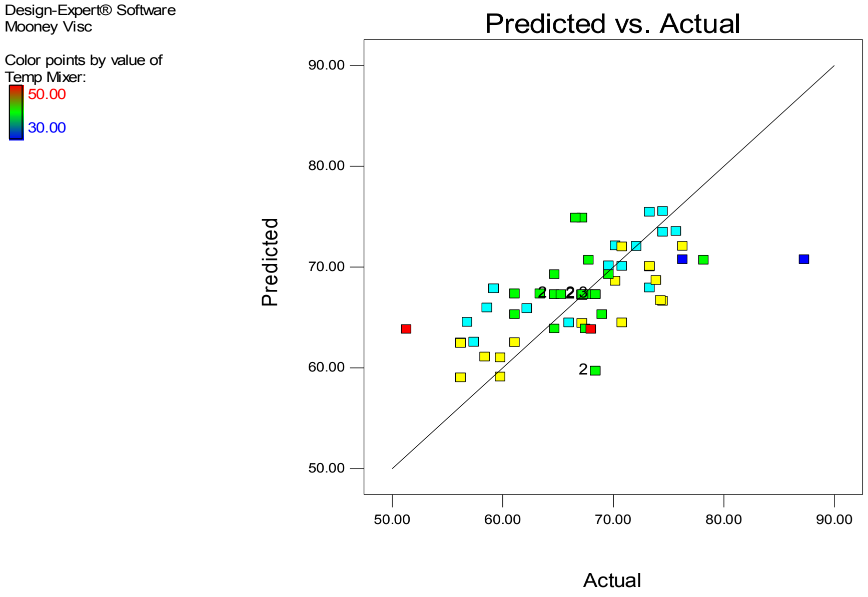


Source: Ebel, Thesis

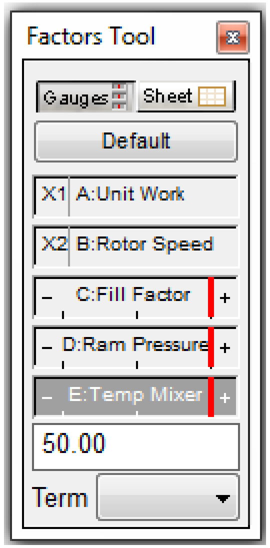
Mixing of SBR:

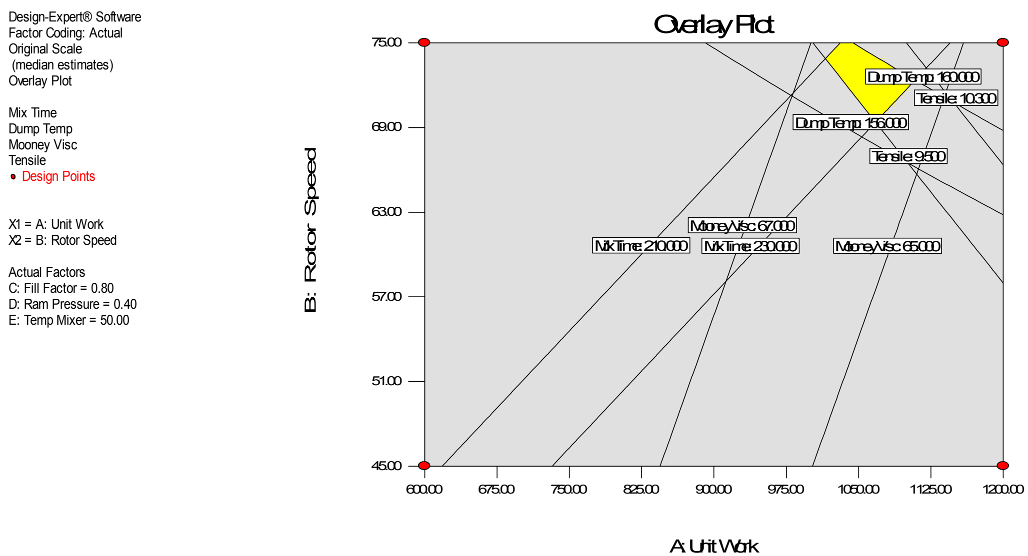
- **Tensile: Predicted versus Actual (left)**
- **Mooney Viscosity: Predicted versus Actual (right)**





Source: Ebel, Thesis

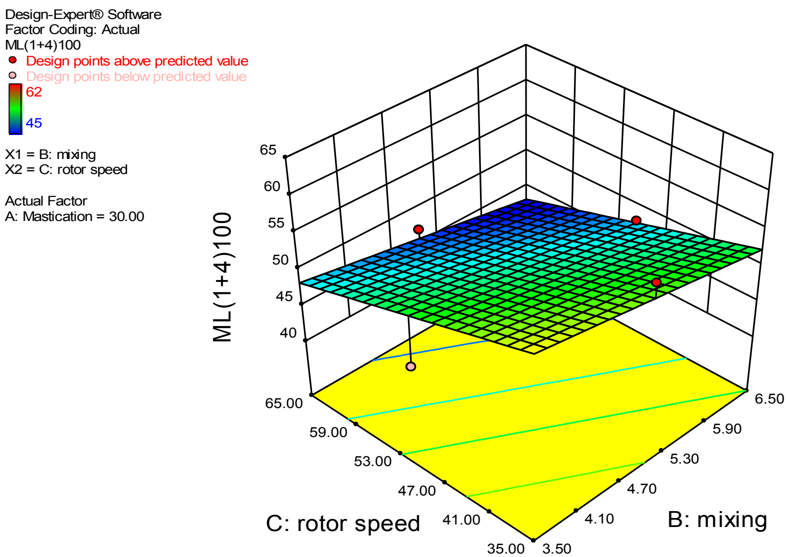


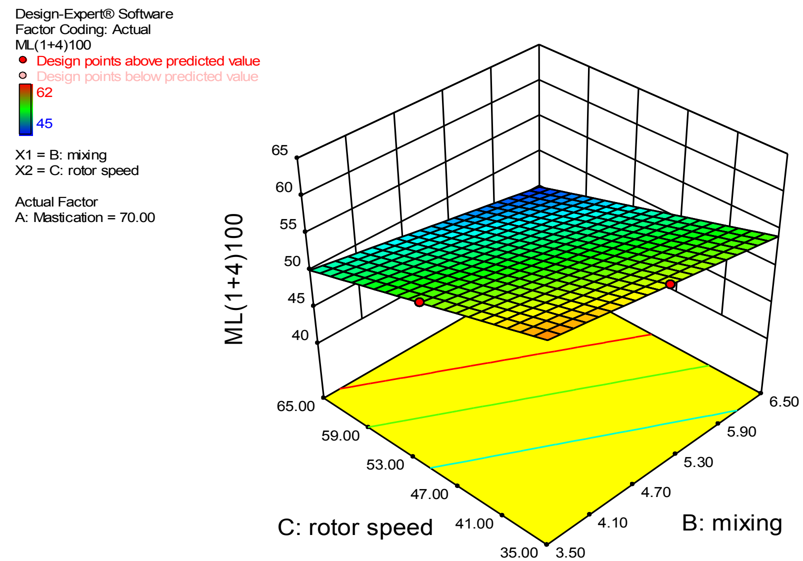


Mixing of SBR: Unit Work over Rotor Speed

- **Tensile at 10.3 MPa (max. value)**
- **Mixing time 210 – 230 sec**
- **Mooney viscosity ML(1+4) 100°C: 65 – 67 Mooney Units**

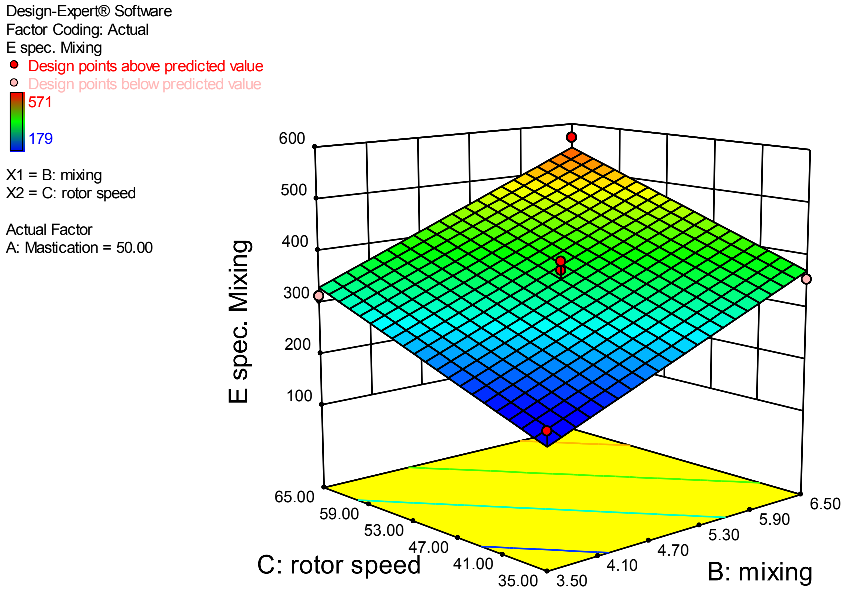
Source: Kreuzwieser, Thesis

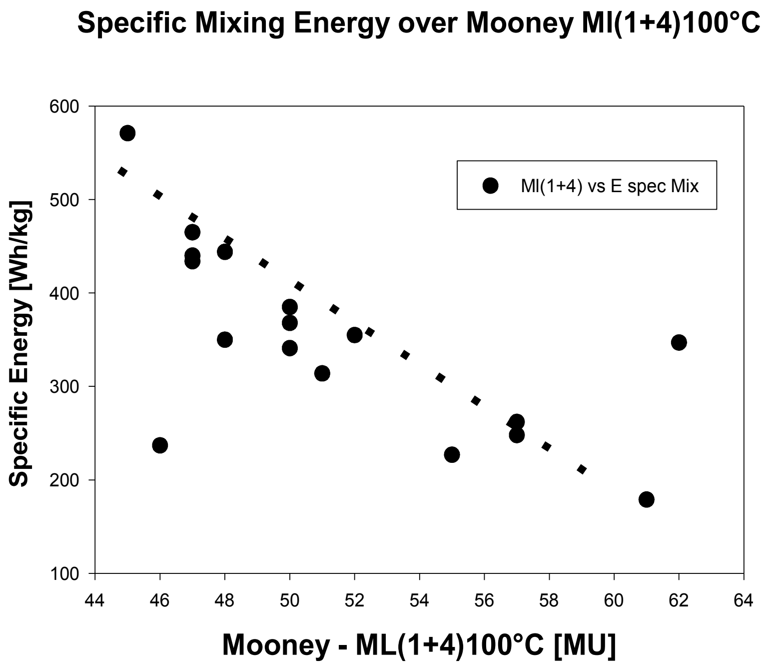




- **Mixing of NR/SBR/BR:**
  - **Ml(1+4)100°C over Mixing Time & Rotor Speed**
  - **Mastication time 30 sec (left) 70 sec (right)**

Source: Kreuzwieser, Thesis

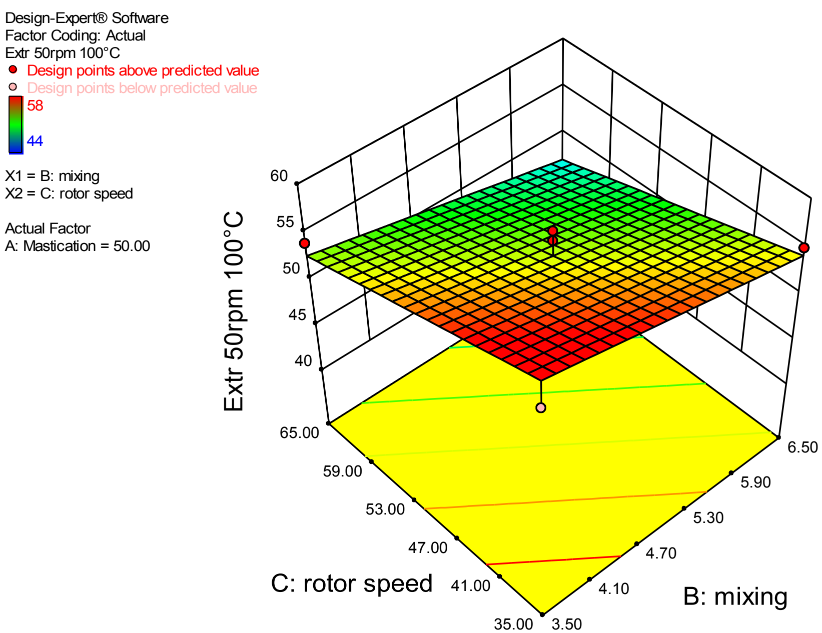


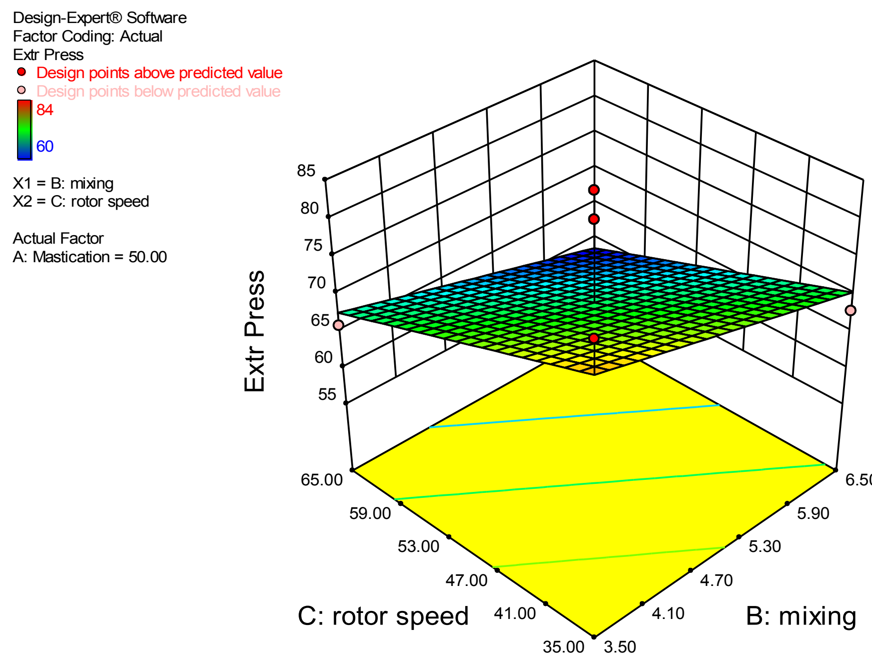


Mixing of NR/SBR/BR:

- **Specific Energy Mix over Mixing Time & Rotor Speed (left)**
- **Correlation of Mooney with Specific Energy Mix (right)**

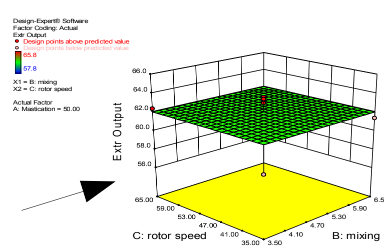
Source: Kreuzwieser, Thesis





Mixing of NR/SBR/BR:

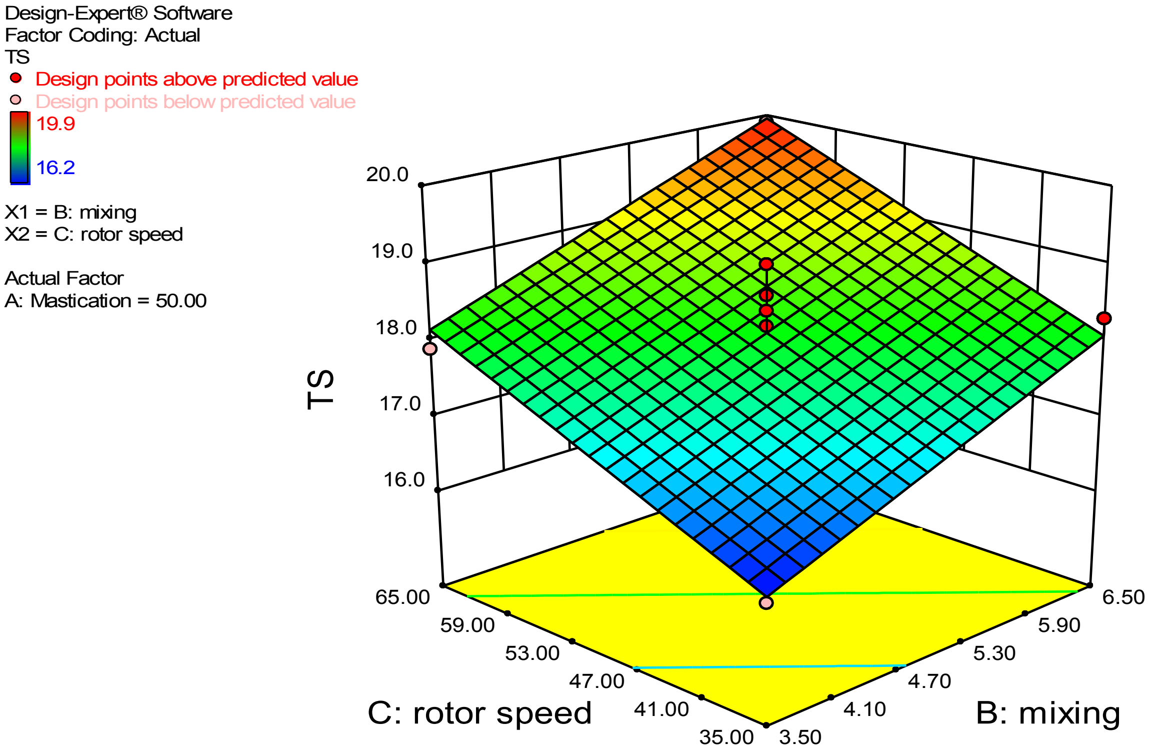
- **Extrusion over Mixing Time & Rotor Speed**
  (Extrusion Experiment at constant Screw speed 50 rpm)
  - **Extrusion Motor power consumption (Nm) (left)**
  - **Extrusion Head Pressure (bar) (right)**
- **Extruder Output at 50 rpm is invariant towards head-pressure.**



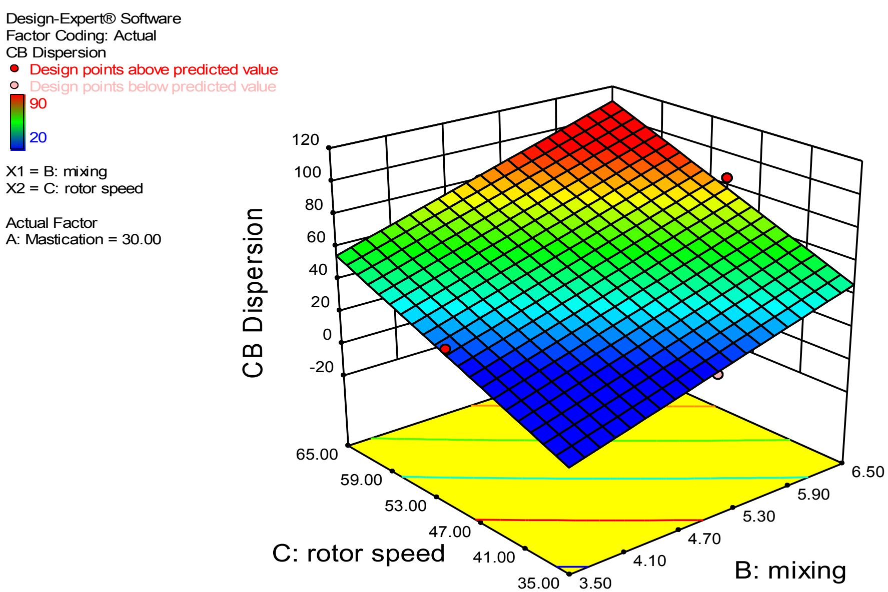
Source: Kreuzwieser, Thesis

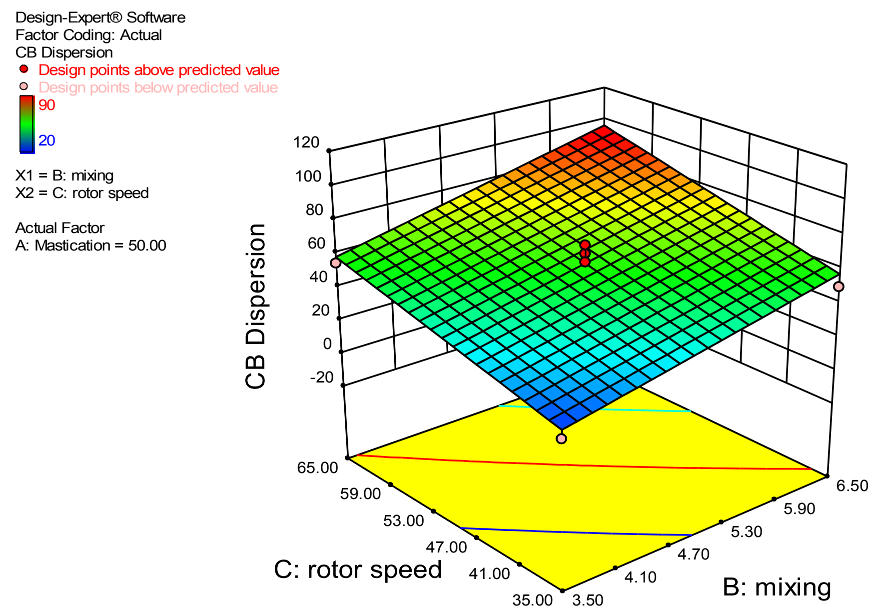
Mixing of NR/SBR/BR:

- **Tensile Strength over Mixing Time & Rotor Speed**
  - **Mastication time has little to none influence**

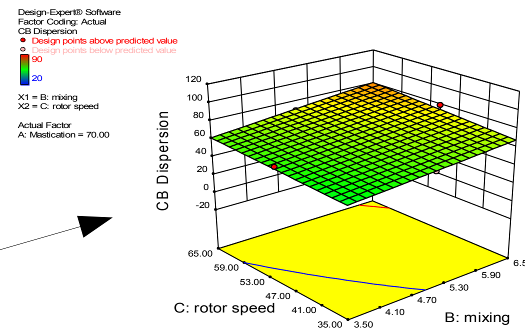


Source: Kreuzwieser, Thesis

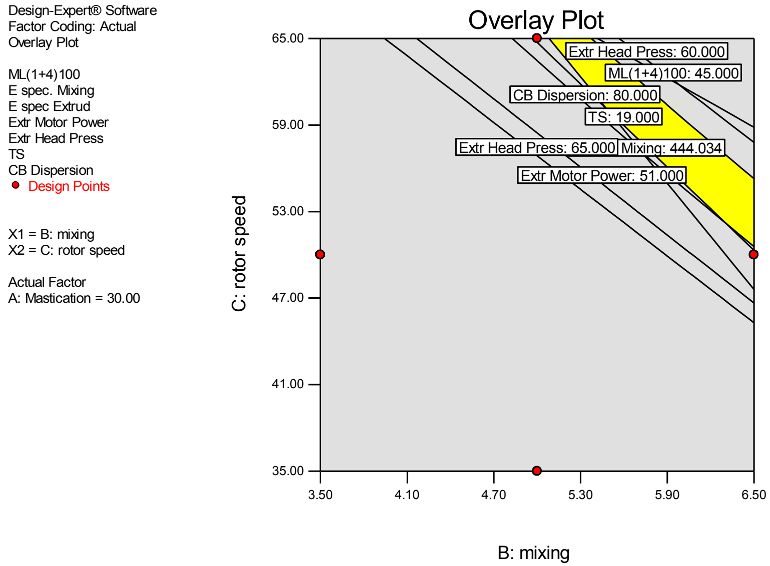


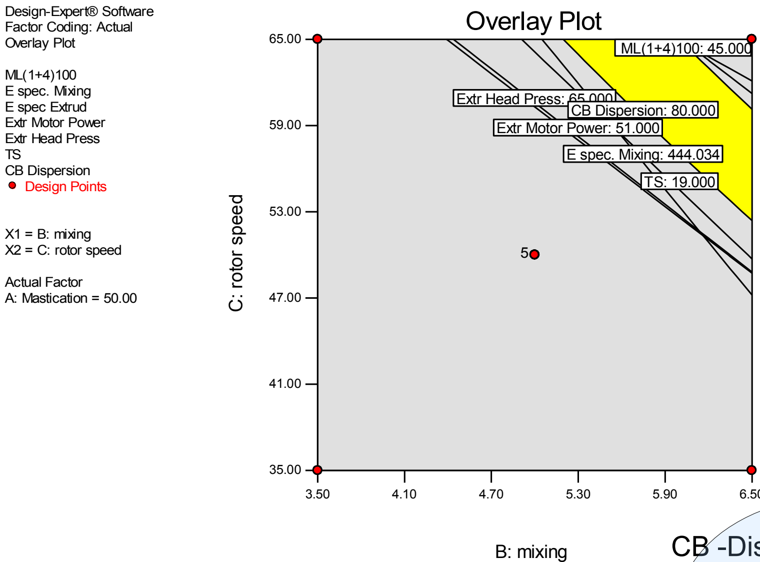


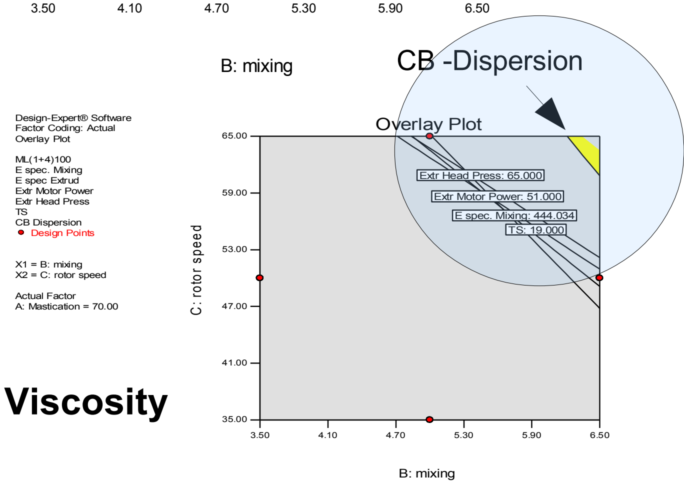
- **Mixing of NR/SBR/BR:**
  - **CB Distribution over Mixing Time & Rotor Speed**
    - **30 sec Mastikation time – (left)**
    - **50 sec Mastikation time – (right)**
      - **70 sec Mastikation time – (lower right)**



Source: Kreuzwieser, Thesis







Mixing of NR/SBR/BR:

- **Factors: Mixing Time over Rotor Speed**
- **Response: Optimization**
  - **Head Pressure / Specific Mixing Energy**
  - **CB- Dispersion / TS (Tensile strength) / Mooney Viscosity**

Source: Kreuzwieser Thesis

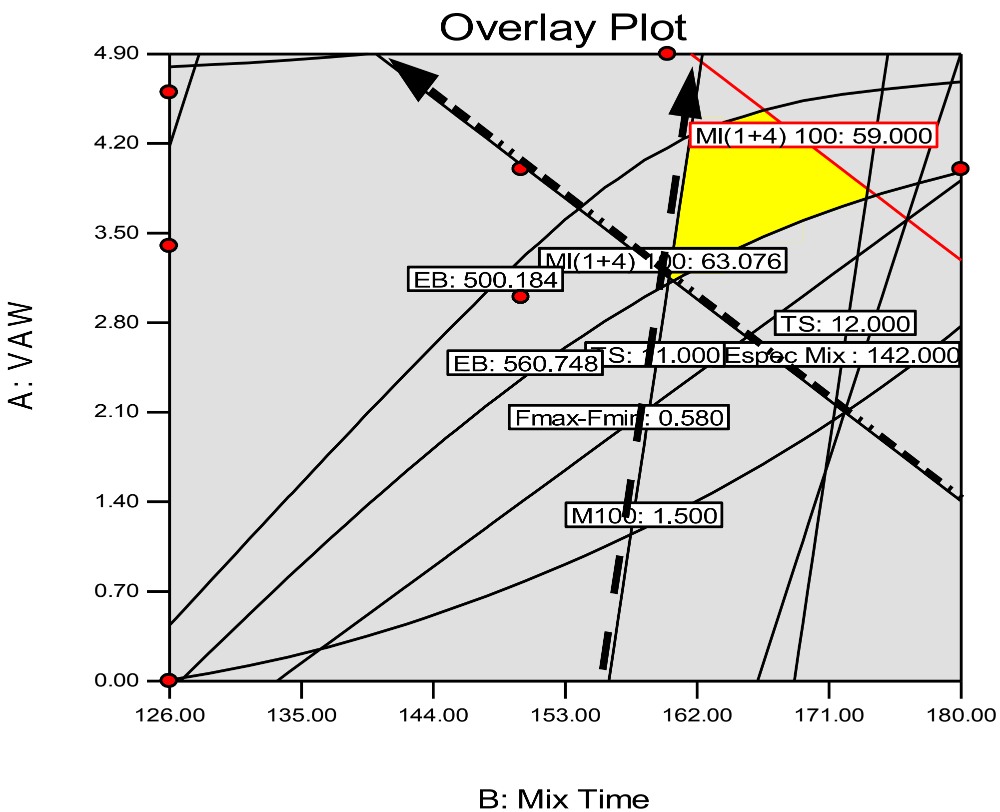
Mixing Time – VAW concentration

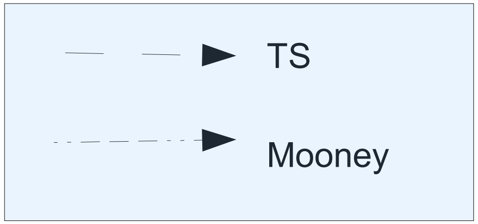
Tire Tread Compound

Design-Expert® Software
Factor Coding: Actual
Overlay Plot

MI(1+4) 100
Fmax-Fmin
Espec Mix
Espec Etrud
M100
M300
TS
EB
Design Points

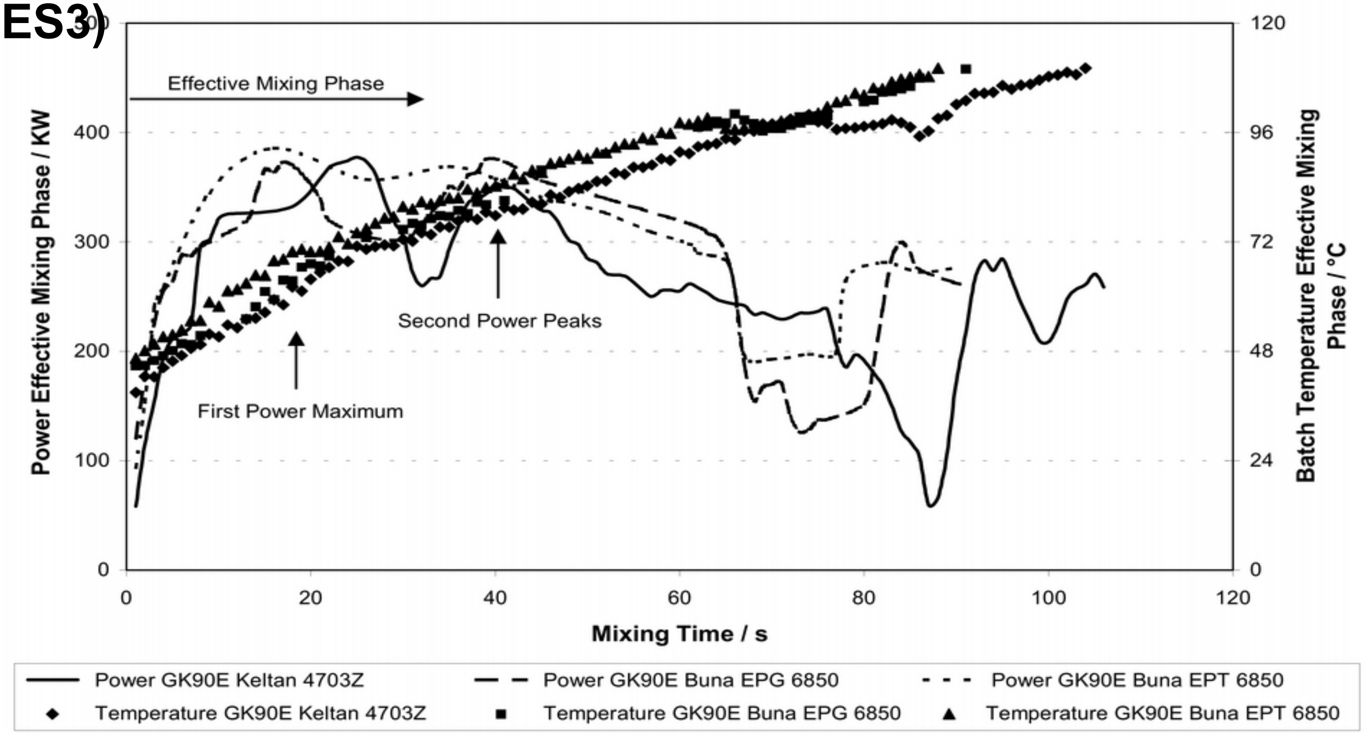
X1 = B: Mix Time
X2 = A: VAW

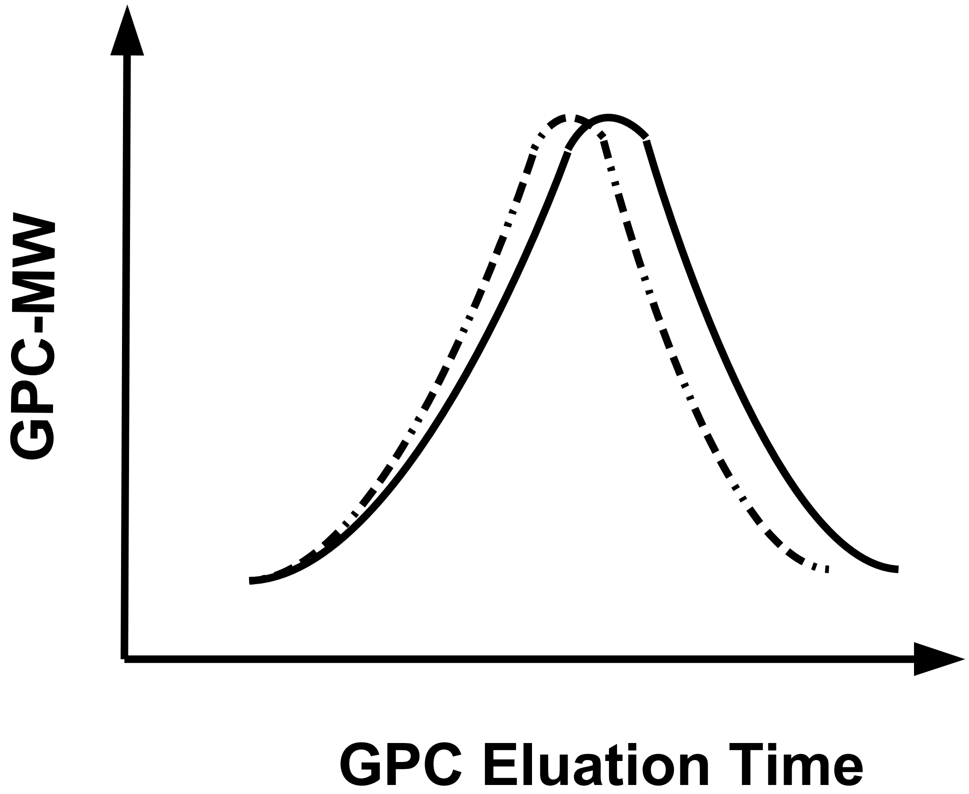




Effect of Polymer Structure on Mixing

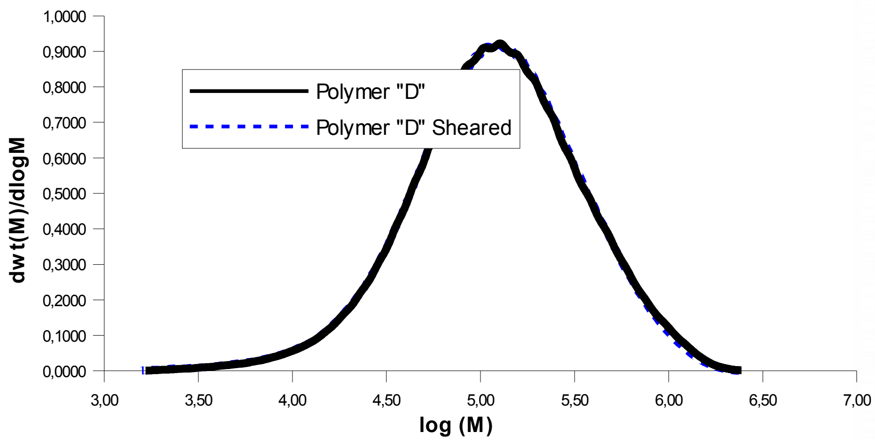
- **Influence of branching**
- **Power consumption of the mixer and batch temperature in the mixing phase due to EPDM LCB (Mixer: W&P, GK90E, Rotor PES3)**

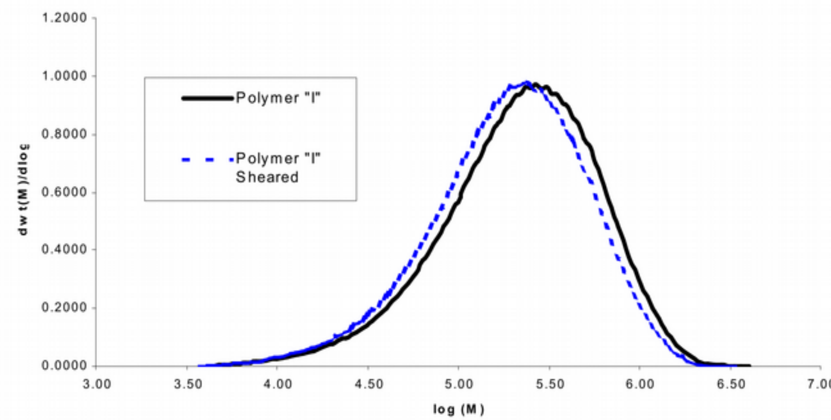




- **Viscosity Drop during mixing**
  - **Mastication of EPDM Change of MW Distribution curve depends on MW and MWD**
    - **Most rubbers show decrease in viscosity, if exposed to mechanical and heat energy.**
    - **Molecular weight curve will change it size and form!**

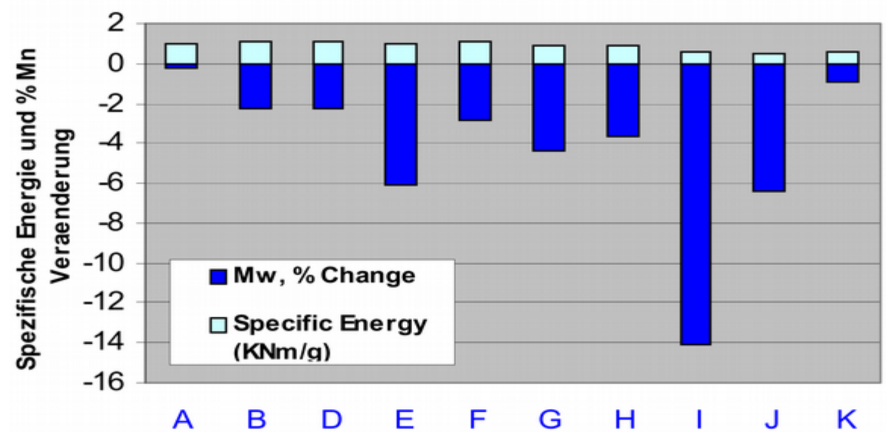
Source: S.Yu, H-J Graf





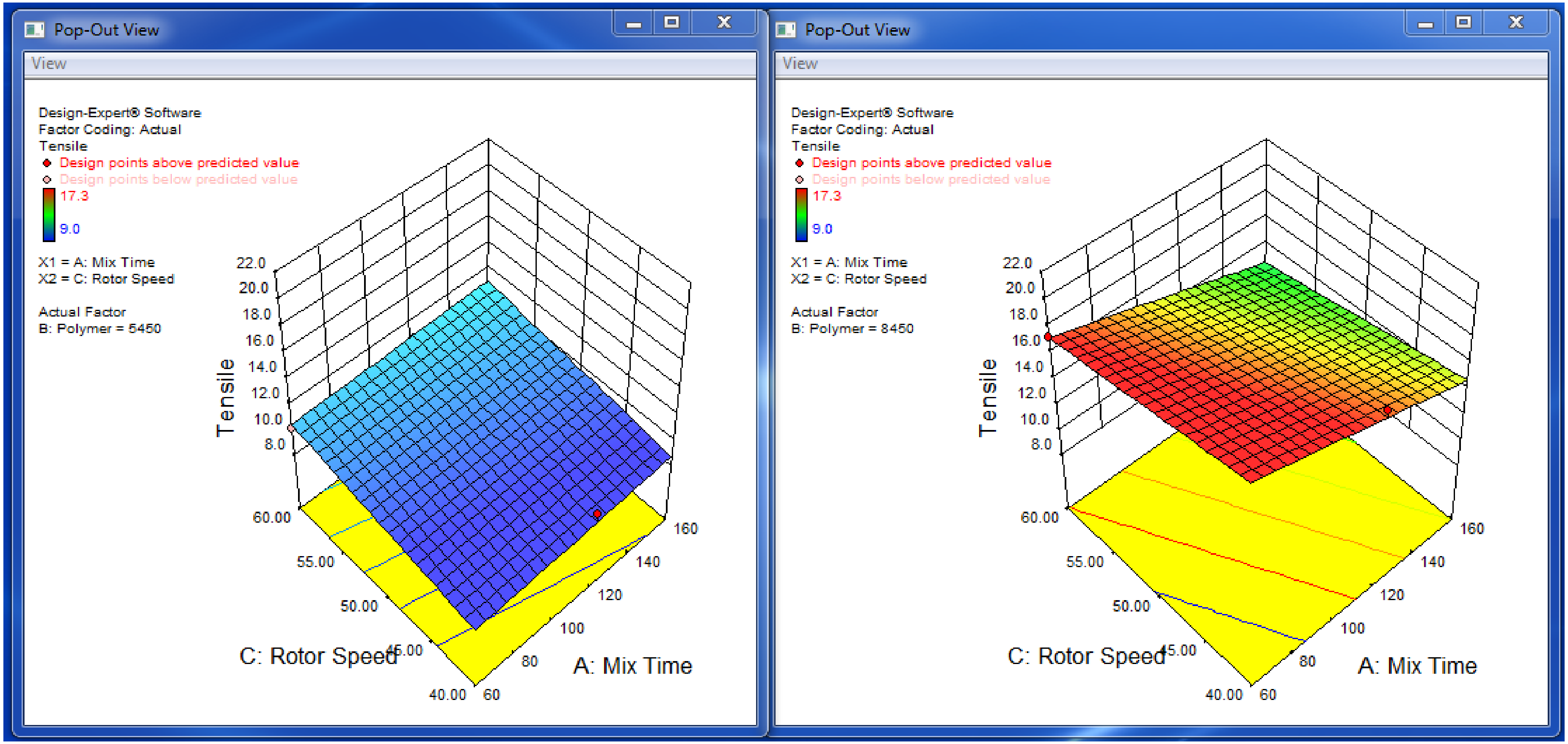
MW decrease of EPDM

- Due to mixing there is a shift of GPC average MW
  (Note the GPC-MW / Mooney Correlation)
- Polymers of different origin behave different
- High MW Polymers effected more than low MW Polymers



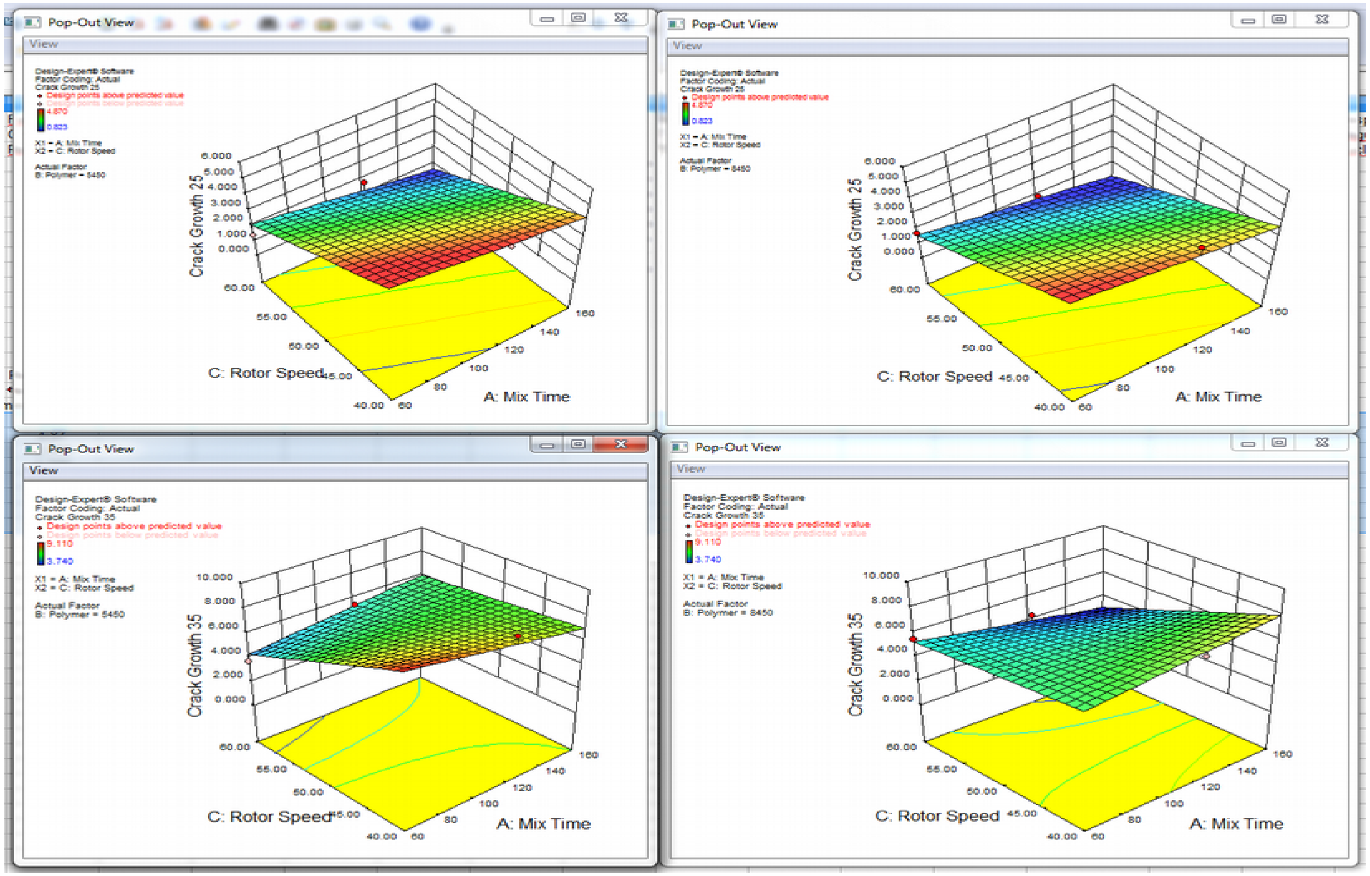
Source: HJ Graf

Mixing experiment with EPDM low (*left*) MW / high MW (*right*) Tensile strength [MPa]



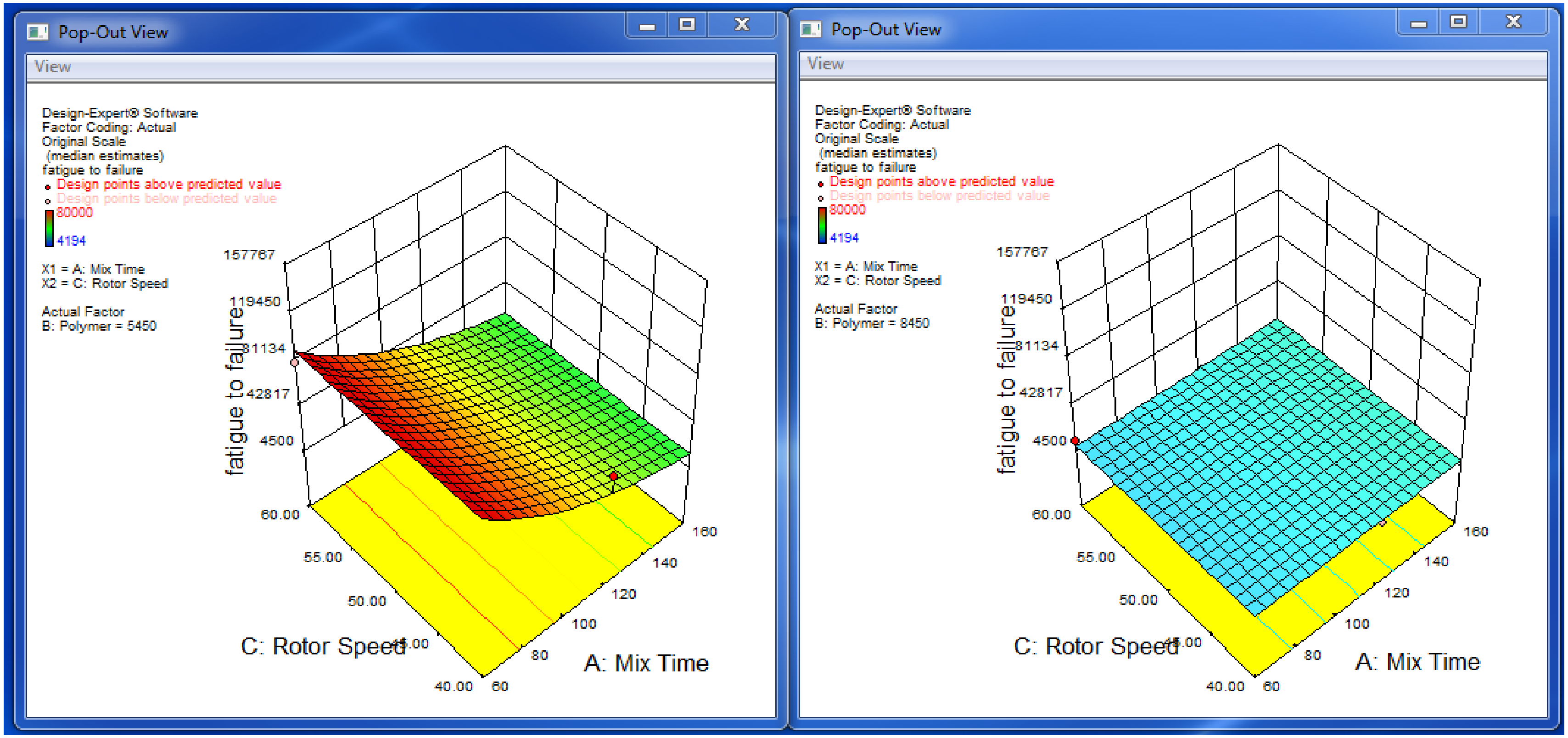
Source: HJ Graf

Mixing experiment with EPDM low (*left*) MW / high MW (*right*)
Crack Growth 25 (*top*) / 35 (*bottom*) (mm/cycle 10^-5)



Source: HJ Graf

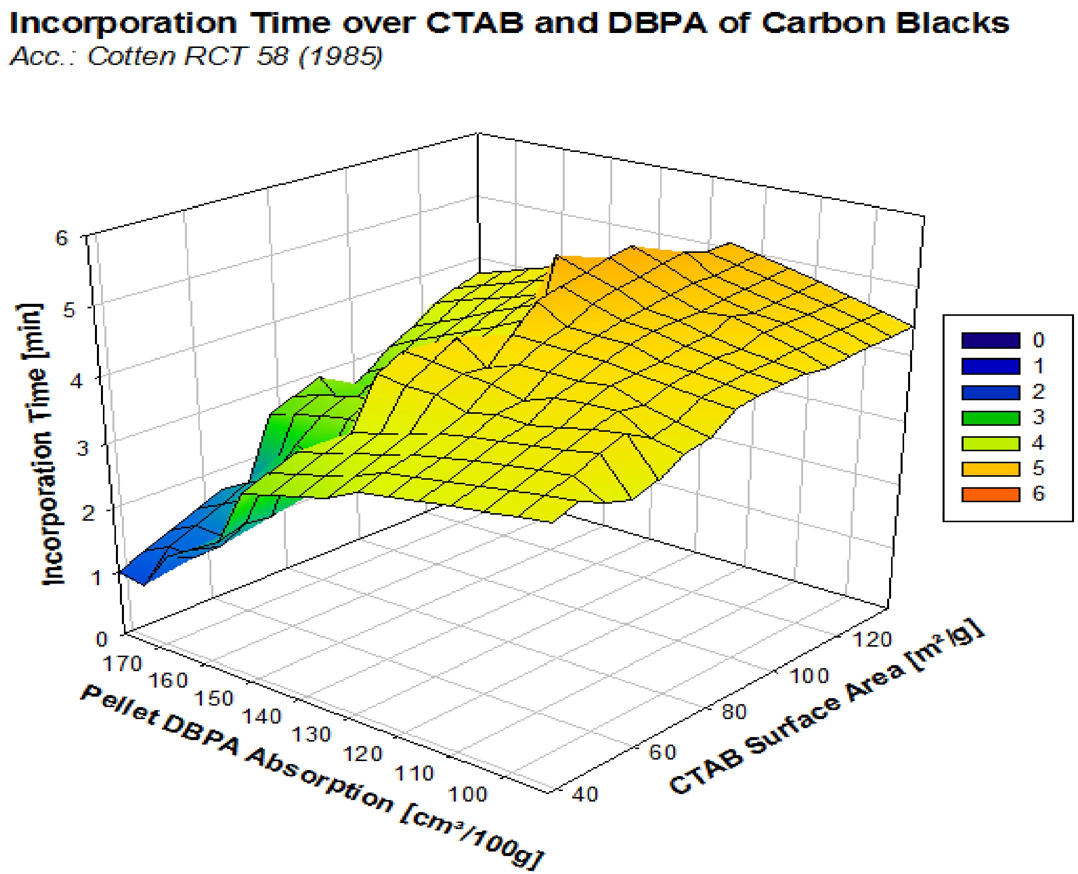
Mixing experiment with EPDM low (*left*) MW / high MW (*right*)
Fatigue to falilure (cycles)



Source: Cotten, RCT 58

Influence of CB Properties

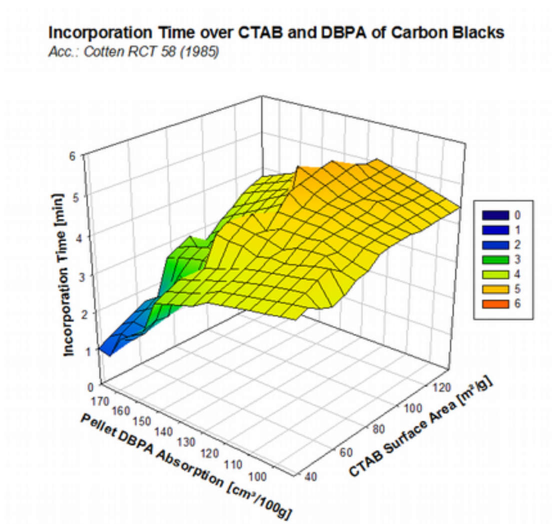
Polymer CB-441 at loading of CB 50 phr

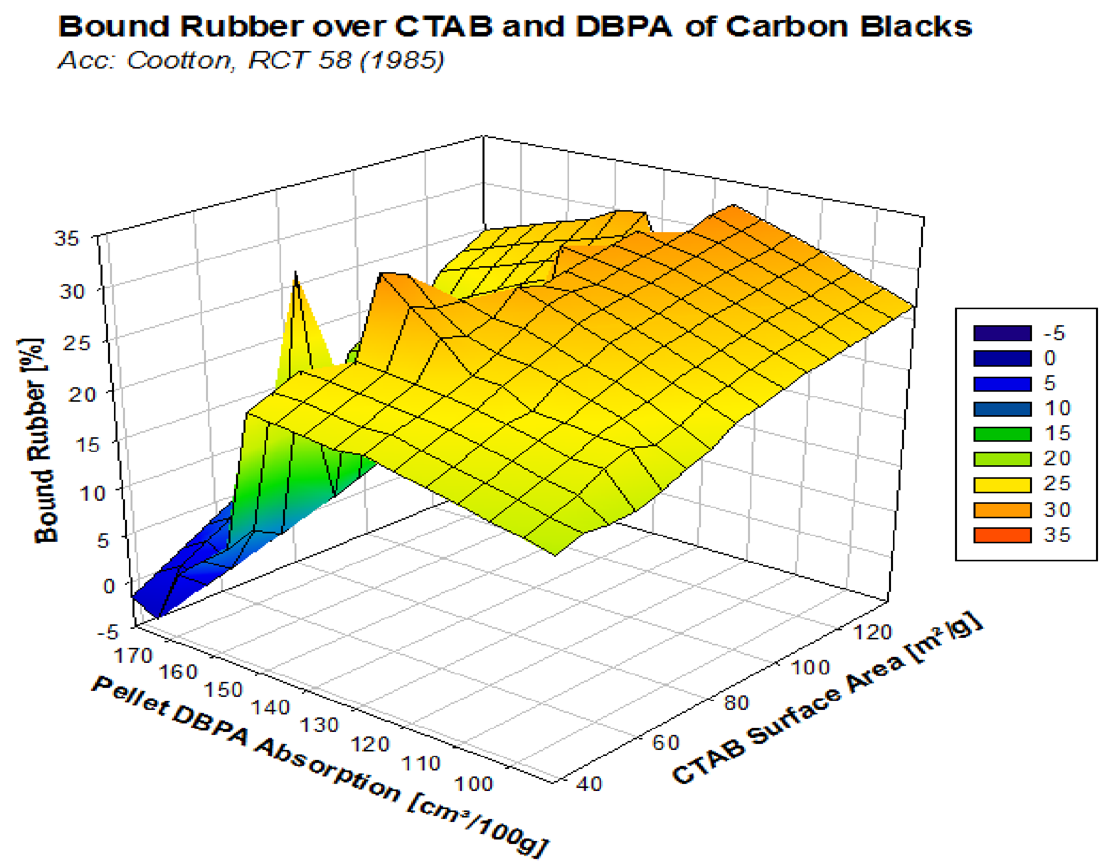


Source: Cotten, RCT 58

Influence of CB Properties

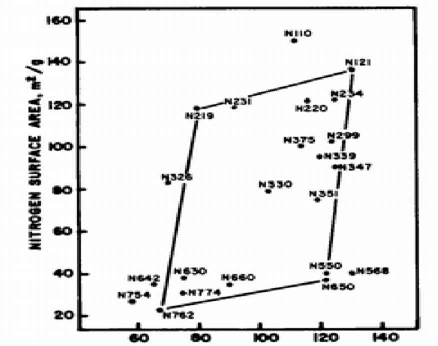
Polymer CB-441 at loading of CB 50 phr

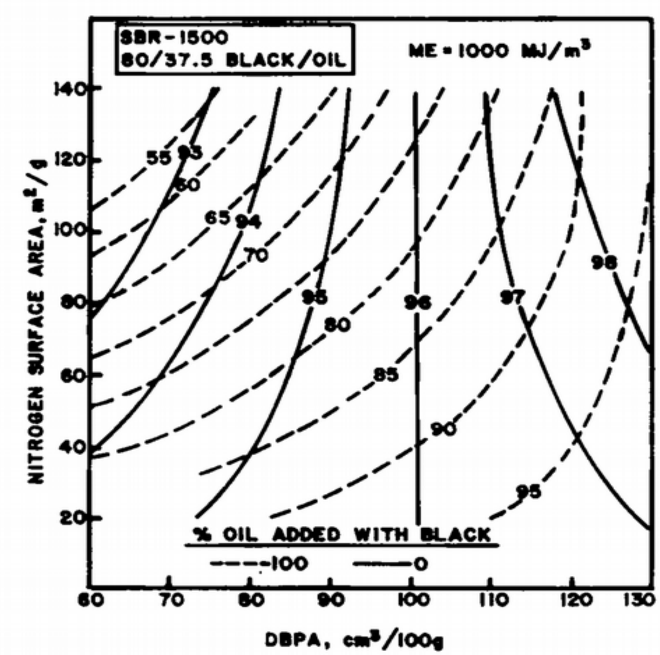




Source: Hess, RCT 57

- **Properties of Carbon Black influence the mixing process and the properties of the compound**
  - **DOE with Carbon blacks**
    - **DOE map according to available CB grades**
    - **CB-Dispersion on SBR 1500 compound as a function of CB surface area and DBPA at to different mixing procedures**
      - **CB and oil added separately**
      - **CB added with black**
      - **SBR 1500 with**
        60 phr CB
        37,5 phr oil
- **According to modern DoE Programs: lack of statistic significance.**



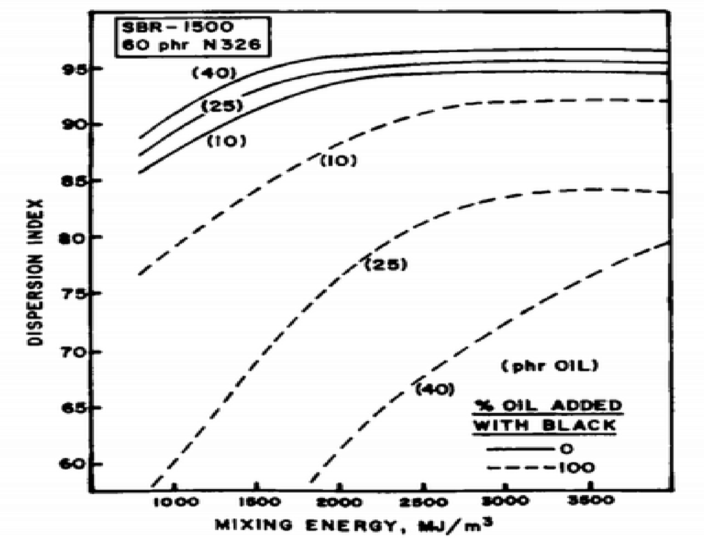


Source: Hess, RCT 57

Addition of Oil

- **In some rubbers oil must be added separately to achieve proper dispersion of CB**
  - **SBR 1500 needs separate addition of oil.**
  - **Otherwise compound will not take up enough shear for dispersion**

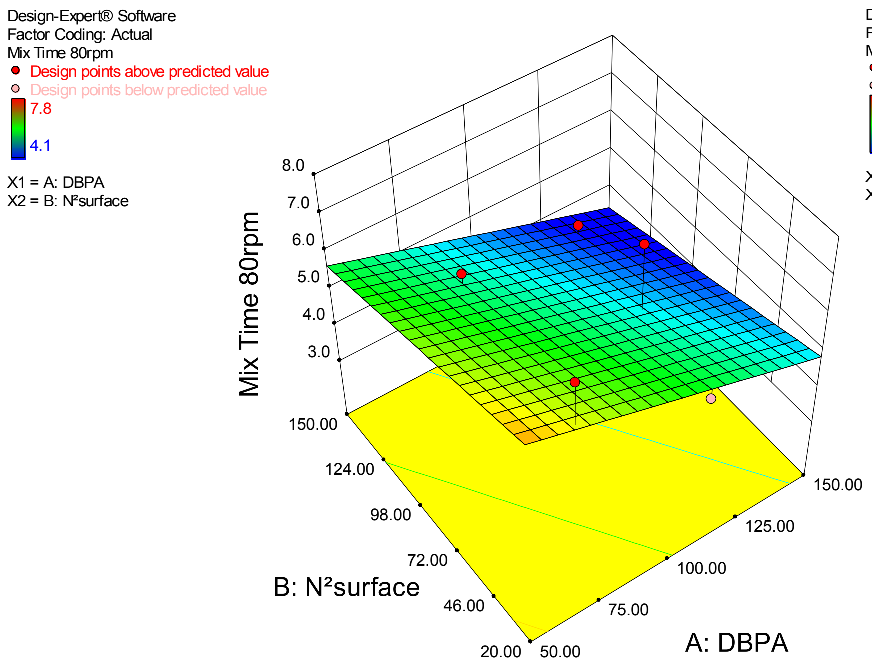
According to modern DoE programs lack of statistic significance

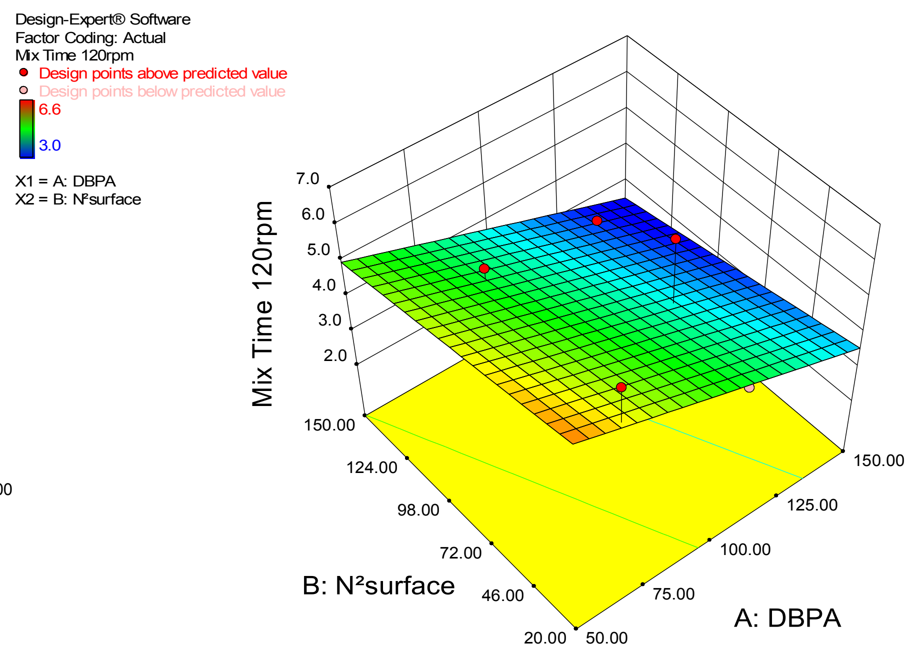


SBR 1500 Compound with 10 phr, 25 phr and 40 phr Oil

SBR 1712 – Mixing dependent on CB DBPA-Absorption & N² Surface

- ***But the Statistic models are not significant***

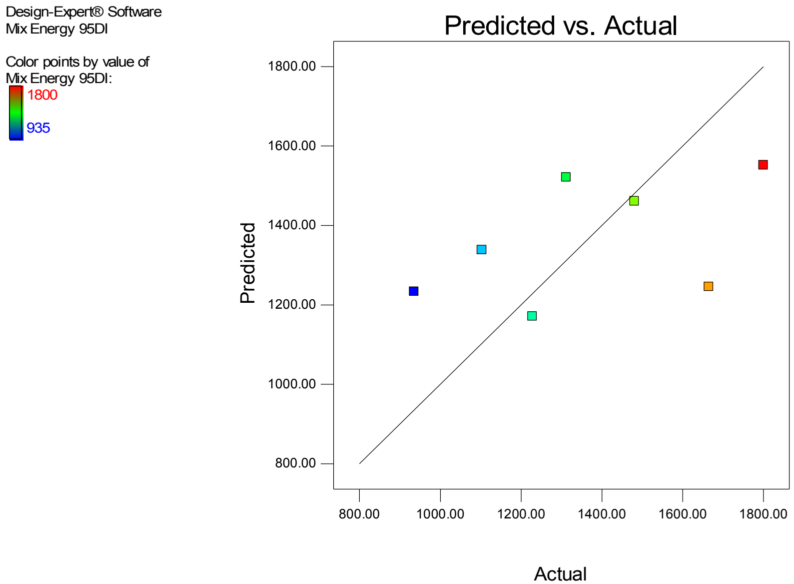


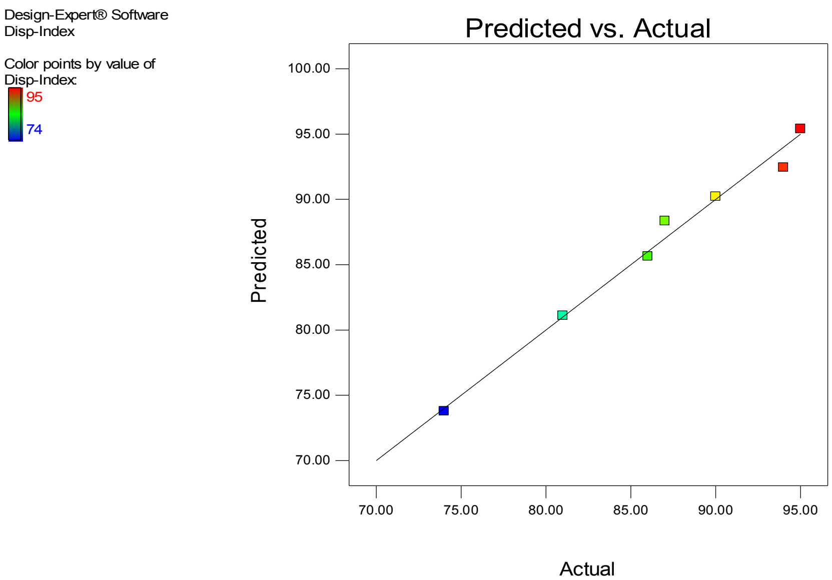


Source: Hess, RCT 57

SBR 1712 – Mixing dependent on CB DBPA-Absorption & N² Surface ???

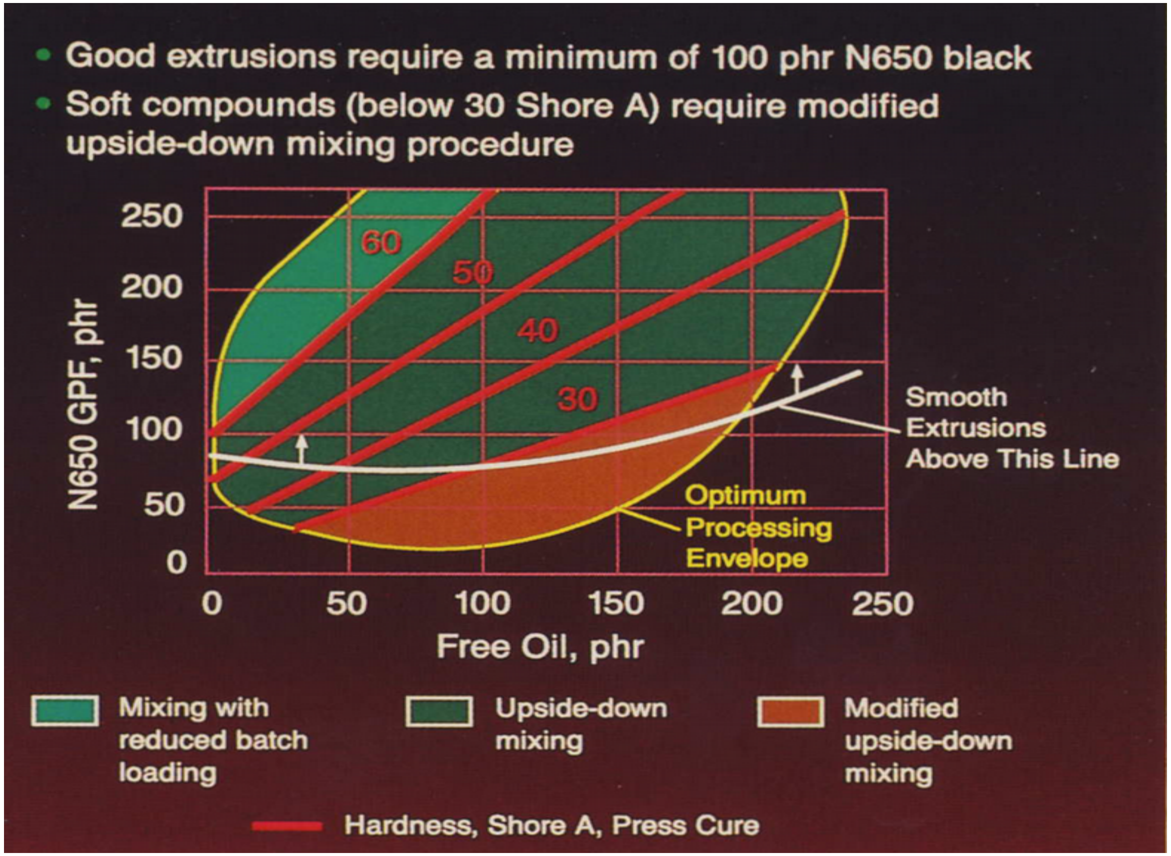
- ***But the Statistic models are not significant***
  - ***Mix Energy to 95% Dispersion – Predicted vs Actual (left)***
  - ***But Correlation of Dispersion Index with Factors are significant (right)***





Filler / Oil ratio of Rubber due to processing window in mixing

- **Viscosity (or MW) dependent ability to load with carbon black and oil**



Conclusion / Important to remember:

- **SBR requires high rotor speed and longer mixing time resp. Energy input**
- **NR (Blend) requires medium to high rotor speed and sufficient time for maximum performance. Temperature should be kept under control**
- **EPDM requires lower rotor speed and mixing time as short as possible**
- **Carbon Black Dispersion experiment should be re developed (statistic significance not sufficient) We should redo this experiments!**