Review of Rubber Mixing
&
Effect on Polymer / Compound Performance

ERIF 2017
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Introduction
Mixing of SBR
Mixing of NR/BR/SBR
Mixing of EPDM
CB Dispersion in SBR
Conclusion

Review of Mixing

Raw materials

Changes in the process of mixing

The behavior of raw materials

Formula

Mixing process

Effects on the process

Forming process

Dr. Hans-Joachim Graf
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
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**
Mixing Diagram Information

- **Ram Down**
  - Mixer under filled
  - Mastication

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

**Graph:**
- **X-axis:** Time (s)
- **Y-axis:** Power supply (kW) and Temperature (°C)
- **Legend:**
  - Power
  - Ram position
  - Avg Power
  - Temperature

Source: Nijmann Vredestein

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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)
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
Mixing of SBR: Mooney Viscosity over Mixing Time *

*) other factors neglected
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)
Mixing of SBR:

Mooney Viscosity over Unit Work & Rotor Speed
(no correction of Ram Pressure & Mixer Temperature & Fill Factor)

- Rotational speed [rpm]
- Unit Work [MJ/m³]
- Mooney viscosity [MU]
Mixing of SBR:

Tensile Strength over Unit Work & Rotor Speed
(no correction of Ram Pressure & Mixer Temperature & Fill Factor)

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

- Tensile: Predicted versus Actual (left)
- Mooney Viscosity: Predicted versus Actual (right)
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
Mixing of NR/SBR/BR:

- $M_{L(1+4)}\text{100°C}$ over Mixing Time & Rotor Speed
- Mastication time 30 sec (left) 70 sec (right)
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Specific Mixing Energy over Mooney ML(1+4)100°C

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

Mixing of NR/SBR/BR:
- Specific Energy Mix over Mixing Time & Rotor Speed (left)
- Correlation of Mooney with Specific Energy Mix (right)

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Mixing of NR/SBR/BR:

λ 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)

λ Extruder Output at 50 rpm is invariant towards head-pressure.

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Mixing of NR/SBR/BR:

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

Design-Expert® Software
Factor Coding: Actual
TS
- Design points above predicted value
- Design points below predicted value

X1 = B: mixing
X2 = C: rotor speed

Actual Factor
A: Mastication = 50.00

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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)
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
Mixing Time – VAW concentration

Tire Tread Compound

Design-Expert® Software
Factor Coding: Actual
Overlay Plot

\( \text{Ml(1+4) 100} \)
\( \text{Fmax-Fmin} \)
\( \text{Espec Mix} \)
\( \text{Espec Etrud} \)
\( \text{M100} \)
\( \text{M300} \)
\( \text{TS} \)
\( \text{EB} \)

- Design Points

\( X_1 = B: \text{Mix Time} \)
\( X_2 = A: \text{VAW} \)

TS
Mooney
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!
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
Mixing experiment with EPDM low (left) MW / high MW (right)
Tensile strength [MPa]
Mixing experiment with EPDM low (left) MW / high MW (right) 
Crack Growth 25 (top) / 35 (bottom) (mm/cycle 10^-5)
Mixing experiment with EPDM low (left) MW / high MW (right)
Fatigue to failure (cycles)
Influence of CB Properties

Polymer CB-441 at loading of CB 50 phr

Incorporation Time over CTAB and DBPA of Carbon Blacks

Acc.: Cotten RCT 58 (1985)
Influence of CB Properties

Polymer CB-441 at loading of CB 50 phr

Bound Rubber over CTAB and DBPA of Carbon Blacks

Acc. Cooten, RCT 58 (1985)
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.
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 1712 – Mixing dependent on CB DBPA-Absorption & N² Surface

But the Statistic models are not significant
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

*Good extrusions require a minimum of 100 phr N650 black*
*Soft compounds (below 30 Shore A) require modified upside-down mixing procedure*
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 redeveloped (statistic significance not sufficient) We should redo this experiments!