Advanced Non-tread Materials for Fuel-Efficient Tires

Lucas Dos Santos Freire, Sr. R&D Engineer (P.I.)
Gina Terrago
PPG Industries, Inc.

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Overview

Timeline

Start: 10/01/2016

End: 09/30/2019

BP2 50% complete

- As of March 2018

Barriers

Technical Target

- Increase tire fuel efficiency by 2% while maximizing key performance properties in non-tread tire components

Technical Barriers

- Reduce petroleum consumption and greenhouse gas emissions
- Meet or exceed vehicle performance and cost expectations

Budget

Total project funding

- $1,143,464 (Total)
- $914,771 (DOE), $228,693 (PPG)

Funding Obligated

- Fully funded

Partners

Akron Rubber Development Lab (ARDL)

Relevance

- **Global Mega-trends affecting Tires: Improve fuel efficiency**
- **Renewed focus on energy loss of non-tread tire components**
  - Equal to or greater than energy loss attributed to the tread
  - Sidewall, relatively high contribution
  - Historically, silica is known to provide degradative resistance benefits
- **Agilon® Performance Silica addresses the challenges of compounding silica in Natural Rubber#**
- **Recent sidewall studies# - partial replacement of carbon black**
  - Hi-Sil® EZ160G-D + *in-situ* silane showed some benefits
  - Agilon® 400G-D showed additional benefits
    - Both manufacturing and performance

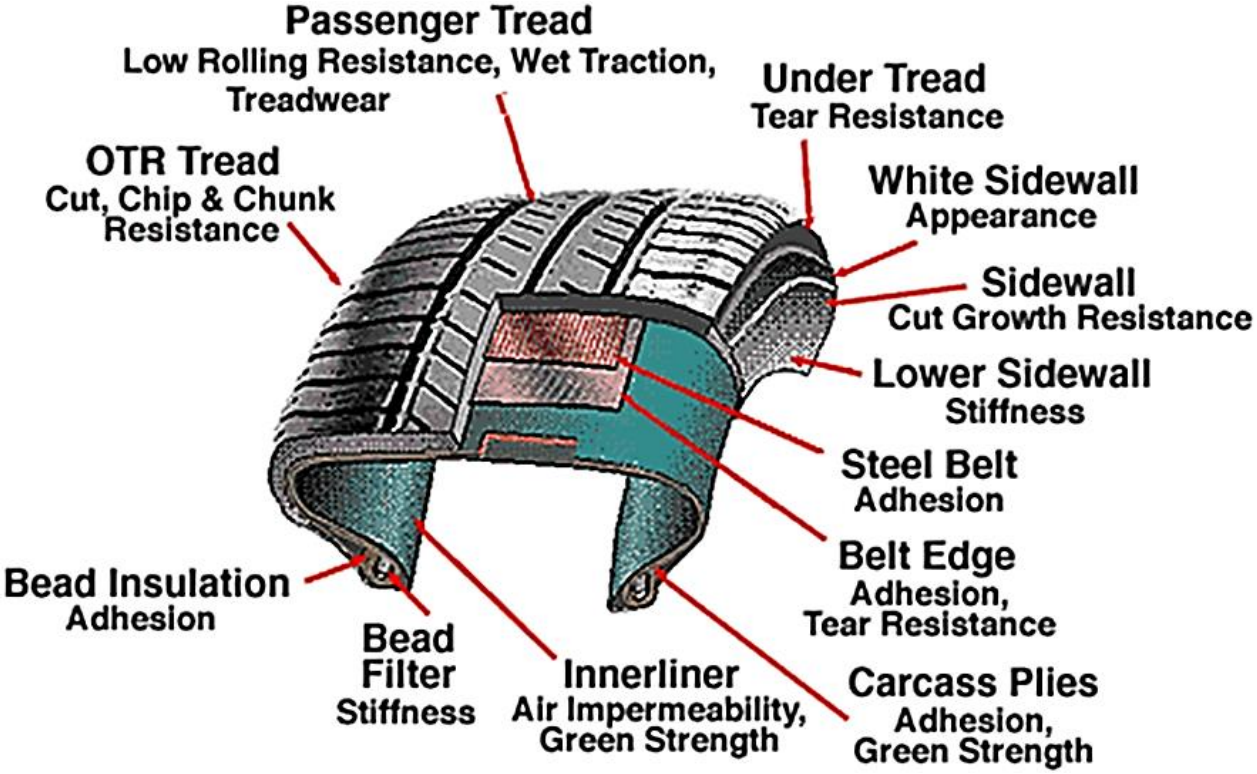
Presented at:

1. Fall 186th Technical Meeting of Rubber Division, ACS, October, 2014
2. Tire Technology Expo 2015, February, 2015
3. Tire Technology Expo 2017, February, 2017

Relevance

Historical Silica Benefits

Several rubber compounds in a tire with different demands and compositions



Renewed Focus ► Energy Loss of Non-Tread Tire Components

- Rolling resistance / Energy Loss ► Fuel Efficiency, Heat Build up, Blow-outs
- Fuel-efficiency: Tread ≈ 50%, Non-tread components ≈ 50%
- **Sidewall reported to be as high as 43% but typically 20% of energy loss**

Relevance

Objective: New silica filler that increases fuel efficiency by 2% while maximizing key performance properties in non-tread tire components compared to current filler system

✓Sidewall initial focus

Scope of work:

✓Document tradeoffs of commercially available fillers

✓Predict and develop optimal reinforcing filler

✓Optimize compound formulation

Key tests/activities from previous period:

- Determined for 10 selected commercial fillers:
  - ✓**Dynamic properties**
  - ✓Impact on **migration / diffusion of antiozonants / antioxidants**
  - ✓Degradative forces including **Ozone resistance**
  - ✓**Electrical resistivity**
- Synthesized prototype fillers with various surface treatments
- Started compound studies with prototype fillers

Approach

- **Focus on sidewall:**
  - ✓ ~20% energy losses ► impacts tire fuel efficiency
    - ➢ 25% energy loss reduction ► ~1% increase in fuel efficiency
  - ✓ Protects other tire components against degradative forces
    - ➢ ≤ 5% degradation resistance loss
  - ✓ Demonstrate with sidewall ► apply to other NR rich non-tread components
    - ➢ Combination achieves goal: 2% better fuel efficiency & best overall performance
- **Silica technology enables better fuel-efficiency, but impact on other key performance properties requires investigation and optimization**
  - ✓ Model sidewall formulation
  - ✓ Evaluate impact of silica morphology and surface chemistry:
    - ➢ Energy loss:
      - ❖ Tan δ, loss modulus, and heat build-up
    - ➢ Degradative forces:
      - ❖ Fatigue to failure, crack growth, abrasion, tear strength, and ozone resistance
      - ❖ Some tests take long time due to aging necessary
    - ➢ Other important criteria:
      - ❖ Processing, extrusion, and curing

Approach

Budget Period 1 – Document Tradeoffs – Existing Materials

- Populate database of performance characteristics tied to the physical/chemical structure of existing filler materials
- Refine the method to characterize migration of antiozonants and antioxidants, and begin to synthesize custom materials to broaden the database in BP 2

Budget Period 2 – Predict and Develop Optimal Reinforcing Filler

- Develop a database with custom-made silica fillers to enable statistical analysis of the results
- Identify the surface chemistry and morphology variables that optimize the wide range of required sidewall performance metrics

Budget Period 3 – Optimize Compound Formulations

- Select the top one or two reinforcing fillers and determine the changes that must be made to a model sidewall formula to best realize the benefits of the new filler

Milestones

MS	Description	Planned	Actual
0.1	ARDL PO in place	12/31/2016	12/13/2016
1.1 2.1.1	Test and commercial baseline filler selection finalized	1/31/2017	12/5/2016
2.1.2	Commercial baseline database generated	7/31/2017	09/01/2017
2.2.1	Tradeoffs in commercial baseline identified	11/30/2017	09/01/2017
3.2.1	Silicas with varying surface chemistry synthesized	11/30/2017	08/01/2017
4.1.1	Database updated for silica surface chemistries	6/30/2018	In progress
4.2.1	Silicas with varying morphology synthesized	8/31/2018	In progress
4.3.1	Database updated for morphology & next gen predicted	10/31/2018	
5.1.1	Next gen synthesized	1/31/2019	
5.2.1	Optimized sidewall formulation determined	7/31/2019	
5.3.1	Improvement Achieved	9/30/2019	

Previous Accomplishments

- **Goal: Develop an improved understanding of the trade-offs associated with commercial reinforcing systems, and what is a statistically significant improvement**

✓ Selected & sourced Carbon Black (3), *Hi-Sil® (4),* and *Agilon ® (3)* fillers

✓ Performed preliminary compounding of fillers to adjust cure state

✓ Verified test protocols with one of each type of filler

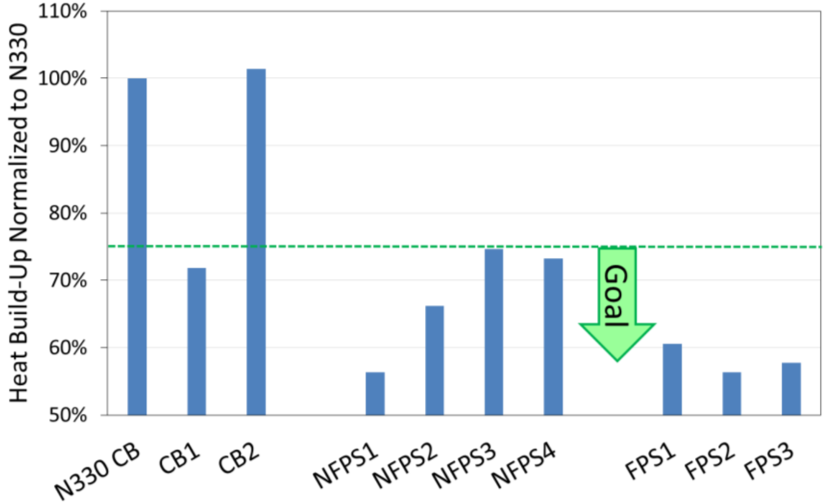
✓ Determined appropriate extraction / migration / diffusion test procedure to use throughout the studies

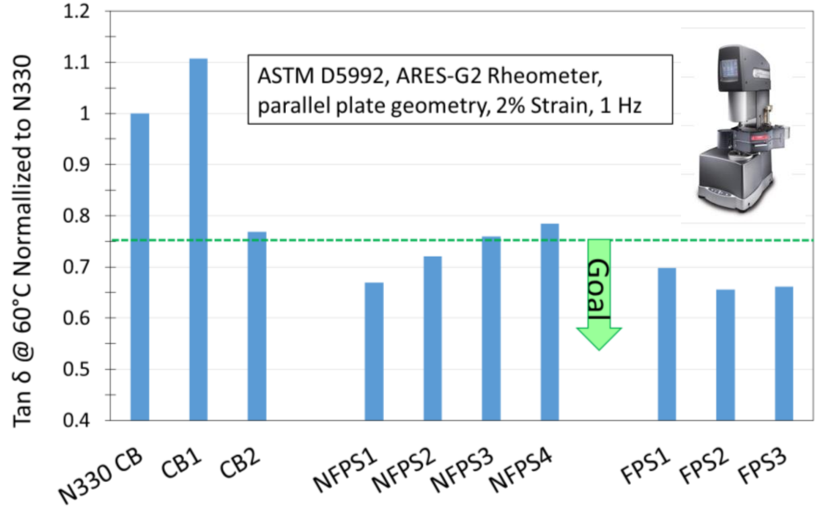
- ➢ Widely-used anti-degradant protection package: Wax + diamine (i.e. 6PPD)
  - ❖ Amines - scavenge free-radicals
  - ❖ Waxes - migrate to surface form protective film
- ➢ Need to optimize reservoir, migration / diffusion rate and surface appearance

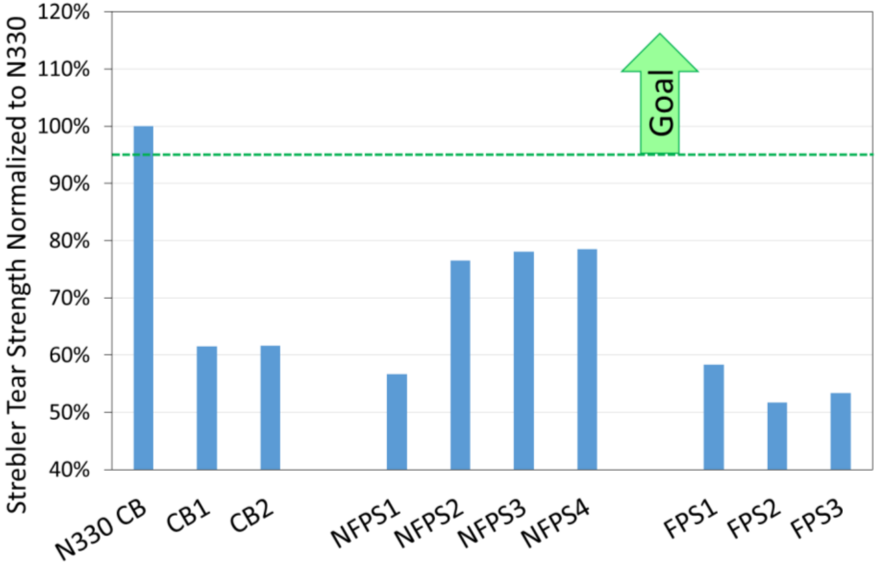
✓ Tests selected

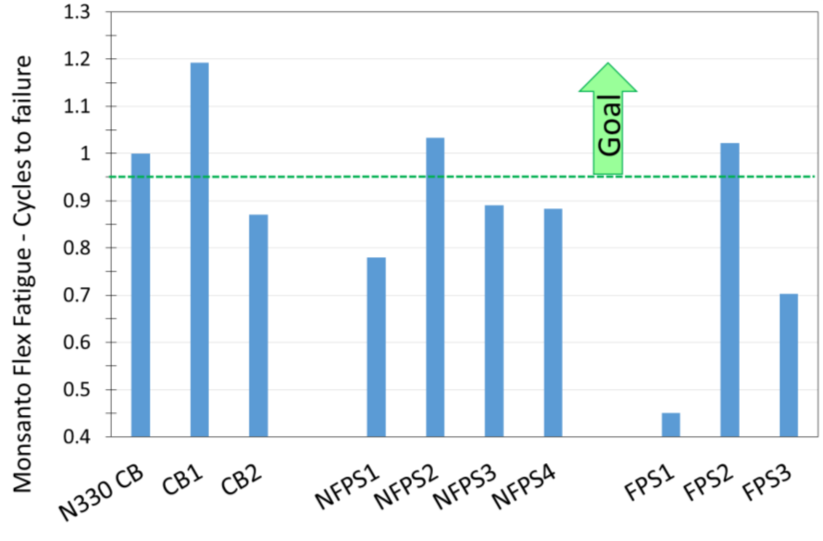
- ➢ Calculate Diffusion (D) constant for 6PPD & Wax
- ➢ Perform heat and light discoloration per ASTM D1148-13
- ➢ Measure 6PPD + wax retention after oven aging of a cured slab
- ➢ Measure 6PPD + wax retention after fatigue testing

Technical Accomplishments – Compound Results



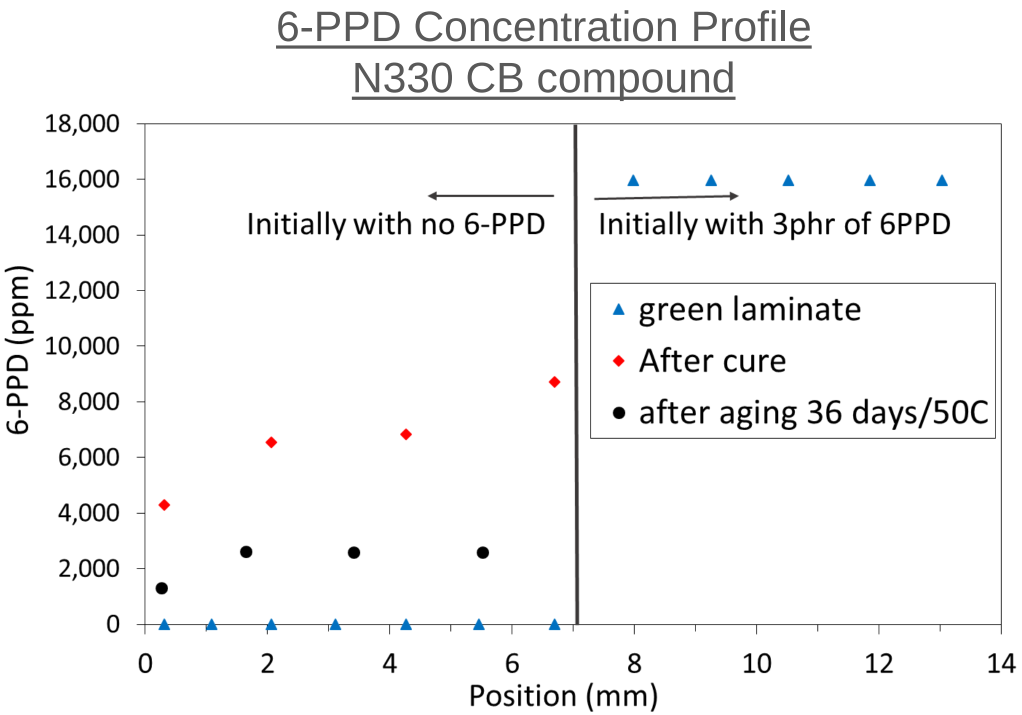






- Silica fillers achieve the 25% energy loss reduction goal
- Tear strength deficient. Compound adjustments could overcome this.
- Flex fatigue trade-offs determined

Antioxidants Migration Studies

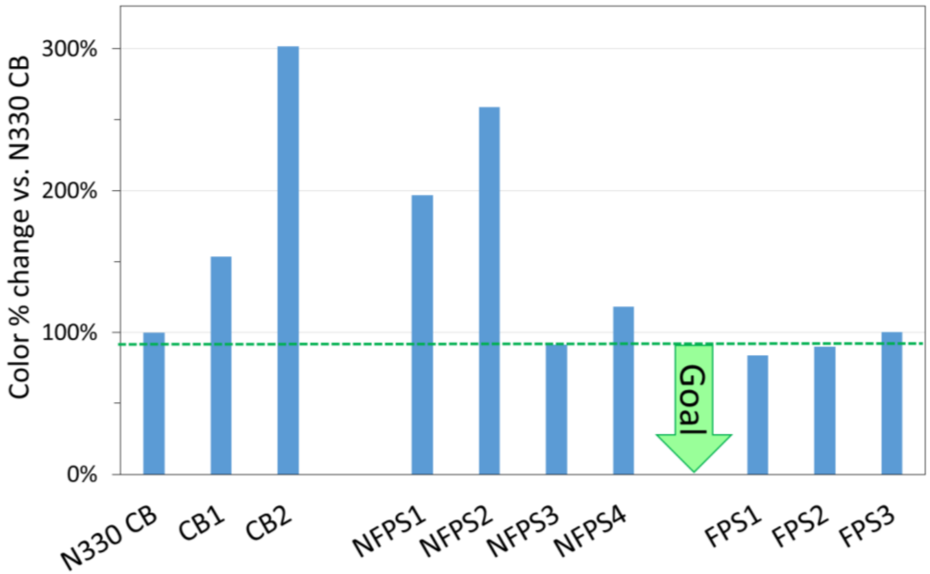


Filler	Diffusion Coefficient (mm^2/min)
N330 CB	6.76
CB1	2.16
CB2	2.16
NFPS1	1.77
NFPS2	0.438
FPS1	5.69
FPS2	1.77
FPS3	1.51

- Diffusion constant measured from samples taken after cure
- Diffusion rate in the order CB > functional silica > non-treated silica
- After aging, 6-PPD finished migration and was partially consumed
- Wax migrated very quickly and homogeneous distribution observed after cure

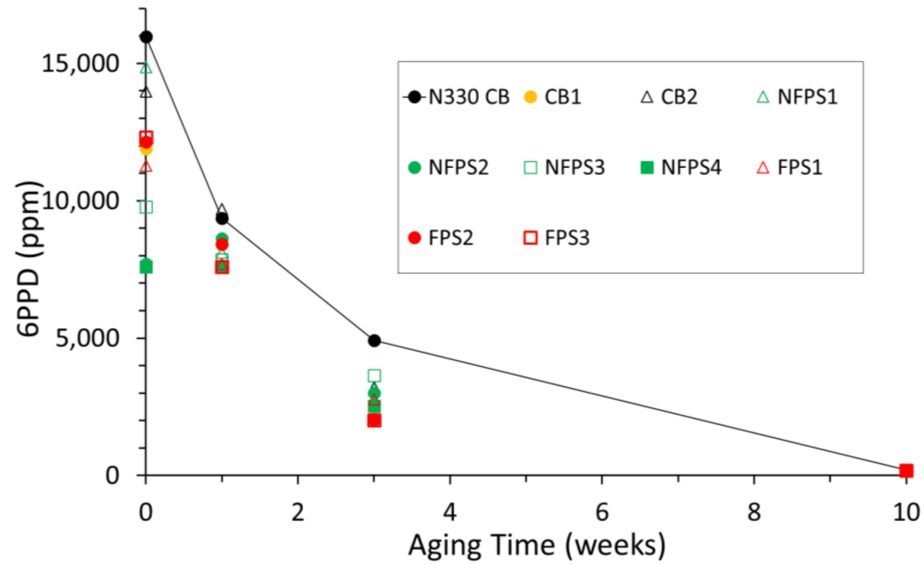
Extraction / Migration / Diffusion Test Procedures

Heat and Light Discoloration



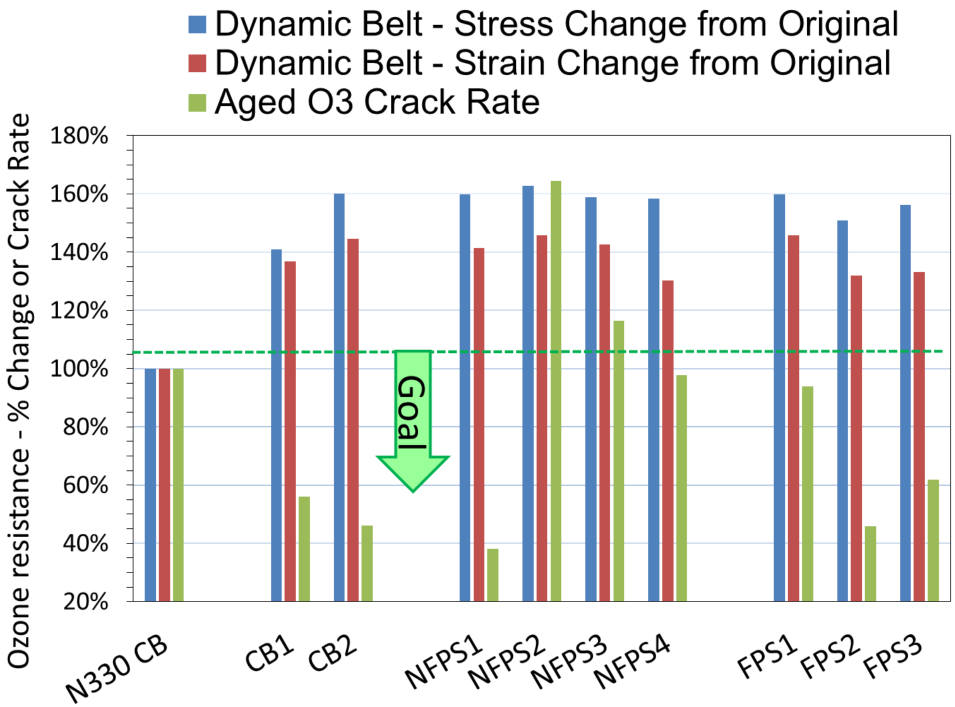
- Compound discoloration due to AO blooming. Some silicas equal or less blooming than CB control

AO Retention After Aging



- Less extractables in silica samples before aging, indicating initial AOs adsorption from silica
- After aging, all samples have about 100ppm of extractable 6-PPD

Ozone Resistance



Some deficiency in ozone resistance observed in some of the ozone tests

Conclusions

- The available commercial silicas show promise in producing an improved overall performance than CB
- Deficiencies of silica technologies were recorded and they provide a starting baseline for BP2

Impact of Novel Silica Surface Chemistries and Morphologies

1. Synthesized ten custom-made silica fillers involving reacting selected chemistries onto the silica surface, holding morphology constant (Milestone 3)
2. Prototype silicas compounded in sidewall formulation

Sample	MDR (160°C)					Garvey Die			
	MH (in-lbs)	ML (in-lbs)	delta torque (in-lbs)	T_c50 (min)	Mooney viscosity	Surface *	Diameter Uniformity*	shrinkage (%)	die swell (%)
TO0517-1NG	10.1	1.3	8.8	3.9	40	5	5	13.5	36.9
TO0517-2NG	10.0	1.3	8.7	3.8	40	5	5	14.8	34.8
N550	**8.6**	**1.1**	**7.5**	**5.8**	**35**	**5**	**5**	**11.7**	**15.2**
TO0517-3NG	10.5	1.3	9.2	8.7	39	5	5	12.7	36.3
TO0517-4NG	9.8	1.3	8.6	8.8	41	5	5	11.5	35.5
TO0517-5NG	9.5	1.3	8.2	8.2	41	5	5	14.3	36.6
TO0517-6NG	8.2	1.2	7.0	7.7	41	5	5	17.0	40.4
TO0517-7NG	8.2	1.2	7.0	8.1	40	5	5	17.2	36.0
TO0517-8NG	8.2	1.3	6.9	7.5	40	5	5	13.2	37.0
TO0517-9NG	9.4	1.2	8.2	6.6	40	5	5	19.7	35.7
TO0517-10NG	9.3	1.1	8.2	5.8	36	5	5	21.0	35.2

- Initial compound data obtained
- CB control compound used to be able to compare to previous data
- Remaining data expected by 05/2018

Response to Previous Year Reviewer Comments

The reviewer wondered how the researchers justify the relationship between tan δ and fuel efficiency.

- Relationship well understood in the tire industry.[a-c]

[a] Advanced Truck And Bus Radial Materials For Fuel Efficiency. DE-EE0006794
[b] The Tyre. Rolling resistance and fuel savings. Michelin 2003. https://community.michelinchallengebibendum.com/docs/DOC-3212
[c] Tires & Truck fuel economy. A new Perspective. Bridgestone. https://commercial.bridgestone.com/en-us/solutions#/?tbr

The reviewer suggested it would be useful if the project team could identify a method to gain tire manufacturers interest in pursuing this technology.

- Goal is to generate data that can be used to persuade tire manufacturers
- Some tire manufacturers already contacted and shown interest in being updated on the progress

The reviewer commented that there is no explanation of the fundamental differences between the formulations of non-tread vs. tread component.

- Several rubber compounds in different tire applications and parts of a tire.

Sidewall:
- composition: 50% NR, 50% BR and highly loaded with antioxidants.
- Demands: high elongation, tear strength, ozone resistance

Collaboration and Coordination with Other Institutions

Akron Rubber Development Laboratory (ARDL)

- Industry recognized vendor conducting testing and analysis
  - ✓ Involved with tire and rubber compound development for over 50 years
  - ✓ Aid rubber industry development efforts by primarily focusing on material science
- Wide range of analytical services, compound development & tire testing
  - ✓ Ability to solve problems and scientific challenges
    - ➢ Adept at conducting failure analysis (damage mode), advanced analytical analysis, and determining root cause mechanisms
  - ✓ Strong background in assessing material robustness, particularly in tires

- For this project provides:
  - ✓ Additional mixing expertise and capacity
  - ✓ Test methods and equipment that PPG does not have in-house
  - ✓ Provides expertise in and conducts migration studies and other testing

Remaining Challenges and Barriers

- Impact of reinforcing prototype filler properties on processing, degradative forces, and energy loss mechanisms of sidewall formulation, as well as impact on the migration/diffusion of antiozonants/antioxidants
  - ✓ What are the trade-offs associated with prototype reinforcing fillers
  - ✓ What is the impact of silica morphology & surface chemistry

- Develop sidewall formulation with a balance of properties
  - ✓ Determine reinforcing silica(s) with optimized morphology & surface chemistry
  - ✓ Determine appropriate combination of curative type and loading, reinforcing filler loading, type of carbon black and carbon black to silica filler ratio, and loading of antioxidant/antiozonant

- Gain tire manufacturers interest in pursuing this technology

Proposed Future Research

- Finish identifying trade-offs in silicas with varied surface chemistries

- Synthesize silicas with varying morphology
  - ✓ Identify performance tradeoffs

- Use overall database to predict optimum filler(s)
  - ✓ Synthesize optimum filler(s)

- Perform systematic sidewall formulation optimization studies with selected optimum filler(s)

- Verify predicted optimum sidewall formulation

Any proposed future work is subject to change based on funding levels

Summary

- Objective
  - ✓ New silica filler increasing fuel efficiency by 2% & maximizing key performance properties in non-tread tire components compared to carbon black
- Expected Outcome
  - ✓ Sufficient lab data to gain tire manufacturers' interest in pursuing technology
  - ✓ 25% tan δ improvement & ≤ 5% decrease in key performance properties
    - ➢ Prefered improved processing and resistance to degradative forces
- Accomplishments
  - ✓ Tests defined and verified
    - ➢ Including quantitative measurement of antidegradant migration / diffusion
  - ✓ Commercial fillers selected and tested
    - ➢ Performance of ten fillers (3 carbon blacks, 4 silicas 3 treated silicas) determined
    - ➢ Ability to meet fuel efficiency improvement verified
  - ✓ Silica fillers with novel surface chemistries synthesized and testing in progress

Technical Backup Slides

Advanced Non-tread Materials for Fuel-Efficient Tires

Background

- PPG: ~$16B, global corporation, founded in Pittsburgh, PA, 1883
  - ✓ World's largest coatings and specialty materials company
  - ✓ Long history of developing silicas for the tire industry
- Industry focus: Improving fuel-efficiency with silica in tire treads
  - ✓ Silica enables reduced mechanical energy dissipation
- Recently PPG developed & patented Agilon® performance silica platform
  - ✓ Addresses issues with conventional silica/in-situ silane systems
- Silica developments for passenger tires driven by the fuel efficiency gains
  - ✓ Same benefits not seen in tire components comprising natural rubber (NR), (i.e. truck and bus radial treads (TBR) or other non-tread compounds)
  - ✓ NR preferred due to resistance to crack growth and tearing
  - ✓ NR contaminants interfere with in-situ silica-silane reaction, yielding poor filler dispersion, tire performance, and processing properties
  - ✓ Silica-silane reaction already complete in *Agilon* products
    - ➢ Improves rolling resistance compared to carbon black in NR compounds
    - ➢ Work published and presented in industry magazines, conferences, and the Annual Merit Review and has been well-received

Black Sidewall

All-rubber component between the tire's bead and tread areas

Outer surface protecting casing against degradative forces

- Ozone, weathering, tear, abrasion, fatigue and cracking

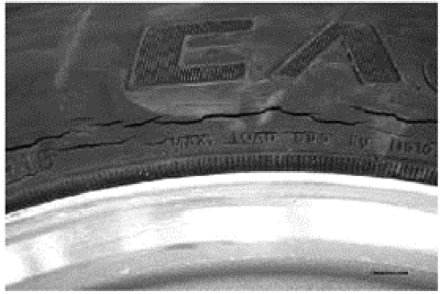
Typical Composition

- 50 / 50 NR and BR
- 40^{+} phr of moderately sized carbon black
- Process oil
- High concentration of antioxidants and antiozonants
- Conventional accelerator-sulfur cure levels

Partial replacement of carbon black with precipitated silica reported to improve performance

- Tear, cut-growth resistance and ozone crack growth resistance
- Potential to reduce hysteretic energy-loss

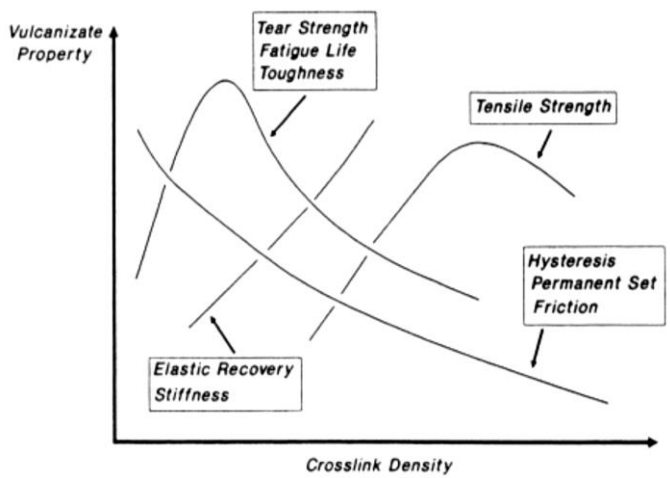
Sidewall Oxidative & Ozone Resistance

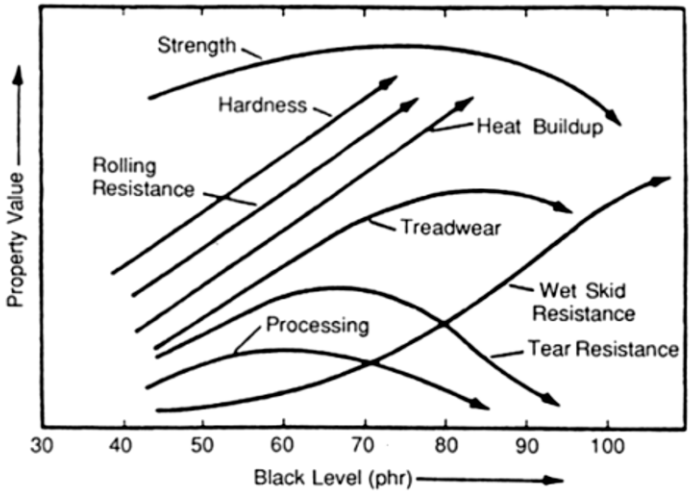


- **Key performance: resist oxidative (O_2) aging & ozone (O_3) attack**
- **Polymers with double bonds in their main chains (i.e. natural rubber and polybutadiene) susceptible to oxidation & ozonolysis**
  - ✓ Key sidewall polymers
- **Exposed surface cracks as material degrades & the chains break**
  - ✓ Elasticity & tensile strength loss ► increased flex-fatigue and ozone cracking
- **Mode of cracking varies between oxygen and ozone attack.**
  - ✓ O_2 ► complex array of shallow crack patterns
  - ✓ O_3 ► deeper cracks aligned at right angles to the tensile strain
- **Wax + diamine most widely-used antidegradant package**
  - ✓ Alkyl-, aryl-disubstituted paraphenylenediamines commonly used
  - ✓ Amines scavenge free-radicals, waxes migrate form surface protective film
  - ✓ Decomposition products discolor the sidewall during service
- **Improvement needed: slow migration and/or reduce discoloration**
  - ✓ No studies investigating ability to improve the lifetime of rubber goods through the rational design of fillers and filler surface chemistry

Balancing Tire Compound Properties

- **Reinforcing filler surface area, structure, polarity & coupling efficiency impact processing, degradative resistance & fuel efficiency**
  - ✓ Changes produce trade-offs in performance
    - ➢ Surface area ► filler-filler & filler-polymer interaction ► tear, crack growth, abrasion resistance, processing and fuel efficiency
    - ➢ Structure ► absorption kinetics ► migration of components to the surface
    - ➢ Surface chemistry ► polarity ► coupling efficiency ► filler-filler & polymer-filler interaction ► abrasion resistance, fuel efficiency, tear and crack growth resistance, antiozonant migration/diffusion
  - ✓ Trade-offs seen with current reinforcing fillers
    - ➢ Carbon black ► non-polar ► polymers low or no polarity ► strong physical adsorption ► polymer molecular mobility ► treadwear
    - ➢ Silica ► polar ► low polymer-filler & high filler-filler interaction ► modify surface with coupling agents ► enables improved balance in treadwear, traction, fuel efficiency





Advantages over Current and Emerging Technologies

- Our approach systematically explores the silica filler design space:
  - ✓ high to low polarity, high to low porosity, high to low surface area, and degree of reactivity with the polymer matrix
- Statistical analysis used to identify key response variables
- Enabled by PPG *Agilon* platform for customizing silica fillers
- Unique to project is studying the interaction between the filler chemistry and ozone cracking resistance
- Expected features and benefits:

Features	Benefits
Decreases hysteresis in sidewall compound	Translates to 1% increase in fuel efficiency per tire (potential for 2% if applied to all non-tread)
Natural Rubber Compatibility	Enables fuel-efficiency in tire compounds that rely on NR, such as sidewalls
Provides better control over ozone degradation and fuel-efficiency improvements in one product	Formulation flexibility for tire manufacturers to optimize performance and cost
Compatible with emerging efficient tire designs, not an either/or solution	Combination with improved tire design can lead to greater fuel efficiency.