Advanced Non-tread Materials for Fuel-Efficient Tires

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Project ID #ACS116

Overview

Timeline

Start: 10/01/2016

End: 09/30/2019

BP1 50% complete

- As of March 2017

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

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
- One component, sidewall, relatively high contribution
- Historically, silica is known to provide degradative resistance benefits

Carbon Black type and/or loading can address energy loss but has a significant negative impact on degradative resistance

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

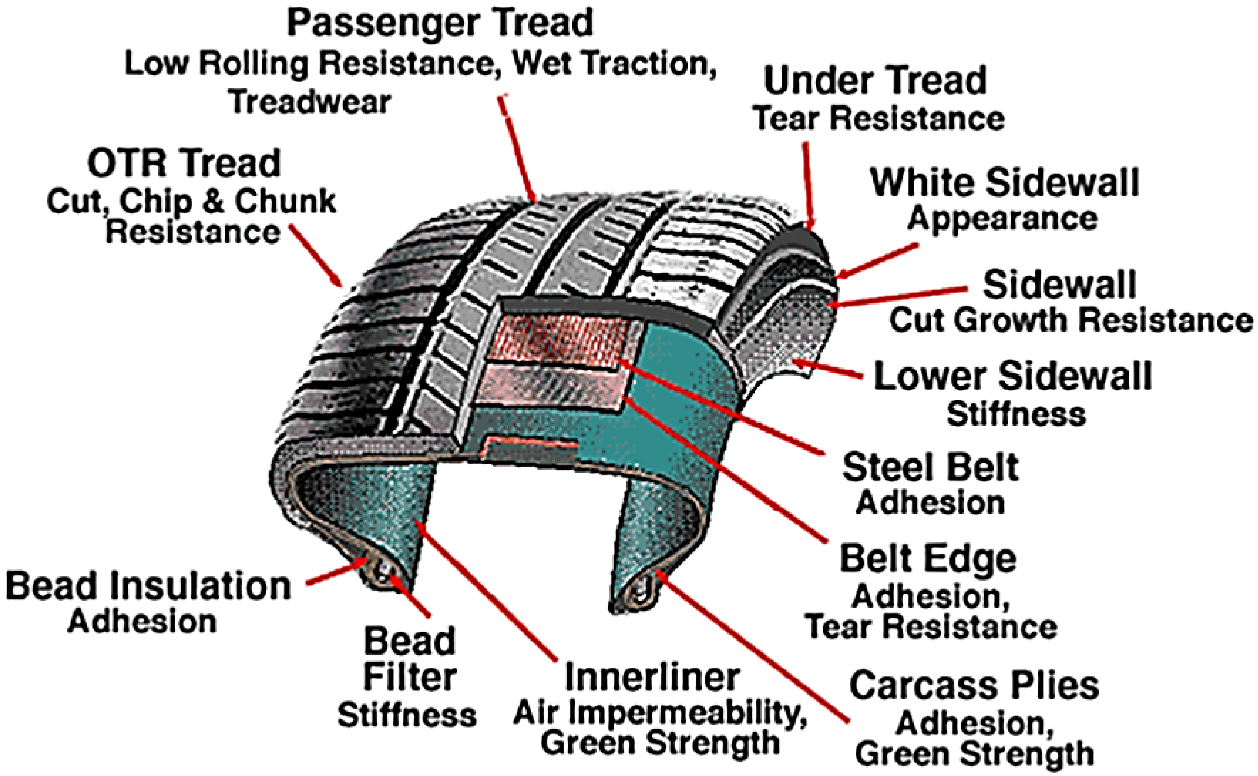
Presented at:

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

Tire Components: Historical and Recent Focus

Historical Silica Benefits



Renewed Focus ► Energy Loss of Non-Tread Tire Components

- Rolling resistance / Rolling loss / 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
  - ✓Predictive model: map filler characteristics to sidewall performance
  - ✓Model compound: ≥ 25% reduced energy loss & ≤ 5% degradation resistance loss
- **Scope of work:**
  - ✓Document tradeoffs of existing materials ❖
  - ✓Predict and develop optimal reinforcing filler ❖
  - ✓Optimize compound formulation ❖
- **Key tests/activities:**
  - ✓Dynamic properties
  - ✓Impact on **migration / diffusion of antiozonants / antioxidants** ❖
  - ✓Degradative forces including **Ozone resistance** ❖
  - ✓**Electrical resistivity** ❖

❖ Information not available from previous studies
❖ Required to obtain tire manufacturer buy-in
❖ Requires specialized equipment / procedures
❖ Requires collaborate effort to obtain in an accurate and timely manner

PPG

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
    - ➢ Fuel-efficiency cannot be increased at the expense of degradative resistance
  - ✓ 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
    - ➢ Other important criteria:
      - ❖ Processing, extrusion, and curing

Approach

Budget Period 1 – Document Tradeoffs – Existing Materials

- Begin populating the 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

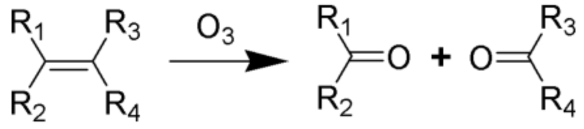
Milestones

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	In progress
2.2.1	Tradeoffs in commercial baseline identified	11/30/2017	
3.2.1	Silicas with varying surface chemistry synthesized	11/30/2017	In progress
4.1.1	Database updated for silica surface chemistries	6/30/2018	
4.2.1	Silicas with varying morphology synthesized	8/31/2018	
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	

Technical Accomplishments

- ## Task 1: Determine Extraction / Migration / Diffusion Test Procedures
  - ✓ Determine the appropriate extraction / migration / diffusion test procedure to use throughout the studies
    - ➢ Widely-used anti-degradant protection combo: 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

- ## Status
  - ✓ 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
  - ✓ Verifying with one each
    - ➢ Carbon black
    - ➢ Hi-Sil® Silica
    - ➢ Agilon® Performance Silica



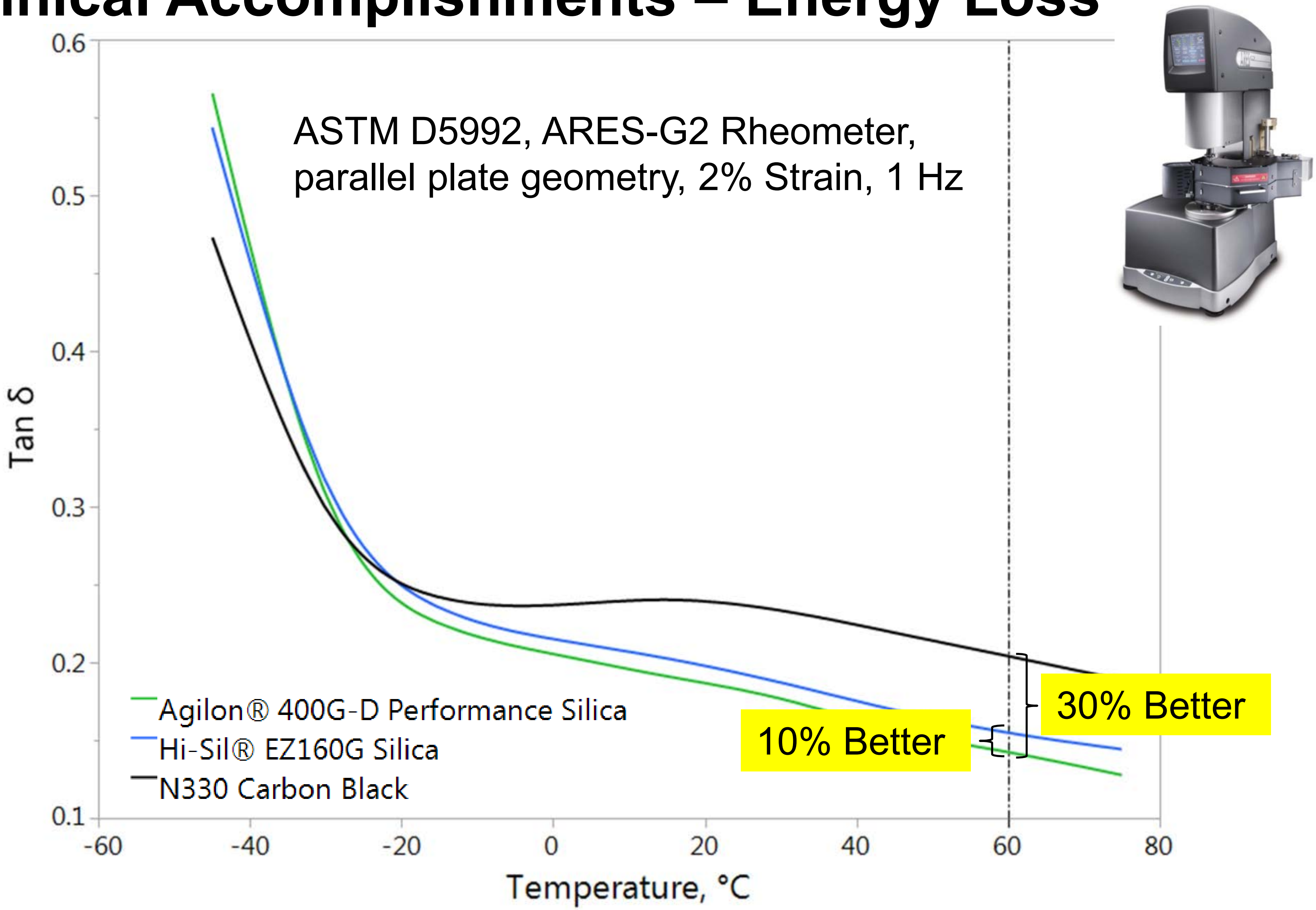
Ozonoloysis is a degradative force that attacks sidewall compounds

Technical Accomplishments

- **Task 2: Baseline - Strengths and Weaknesses of Commercial Reinforcing Filler Systems**

- **Status**
  - ✓ Carbon Black (3), *Hi-Sil (4),* and *Agilon (3)* fillers selected & sourced
  - ✓ Completed preliminary compounding for all ten fillers to adjust the curatives to get a similar cure state
  - ✓ Completed compounding ten fillers with adjusted formulation
    - ➢ Verified most test protocols with one Carbon Black, *Hi-Sil,* and *Agilon* filler
      - ❖ Ozone test protocols being verified
    - ➢ Testing of remaining fillers using verified protocols has started
  - ✓ Electrical surface resistivity was identified as an additional property that should be monitored in this program
    - ➢ Solutions to surface resistivity are not directly part of the program, but may be considered during BP #3 as we optimize the sidewall formulation

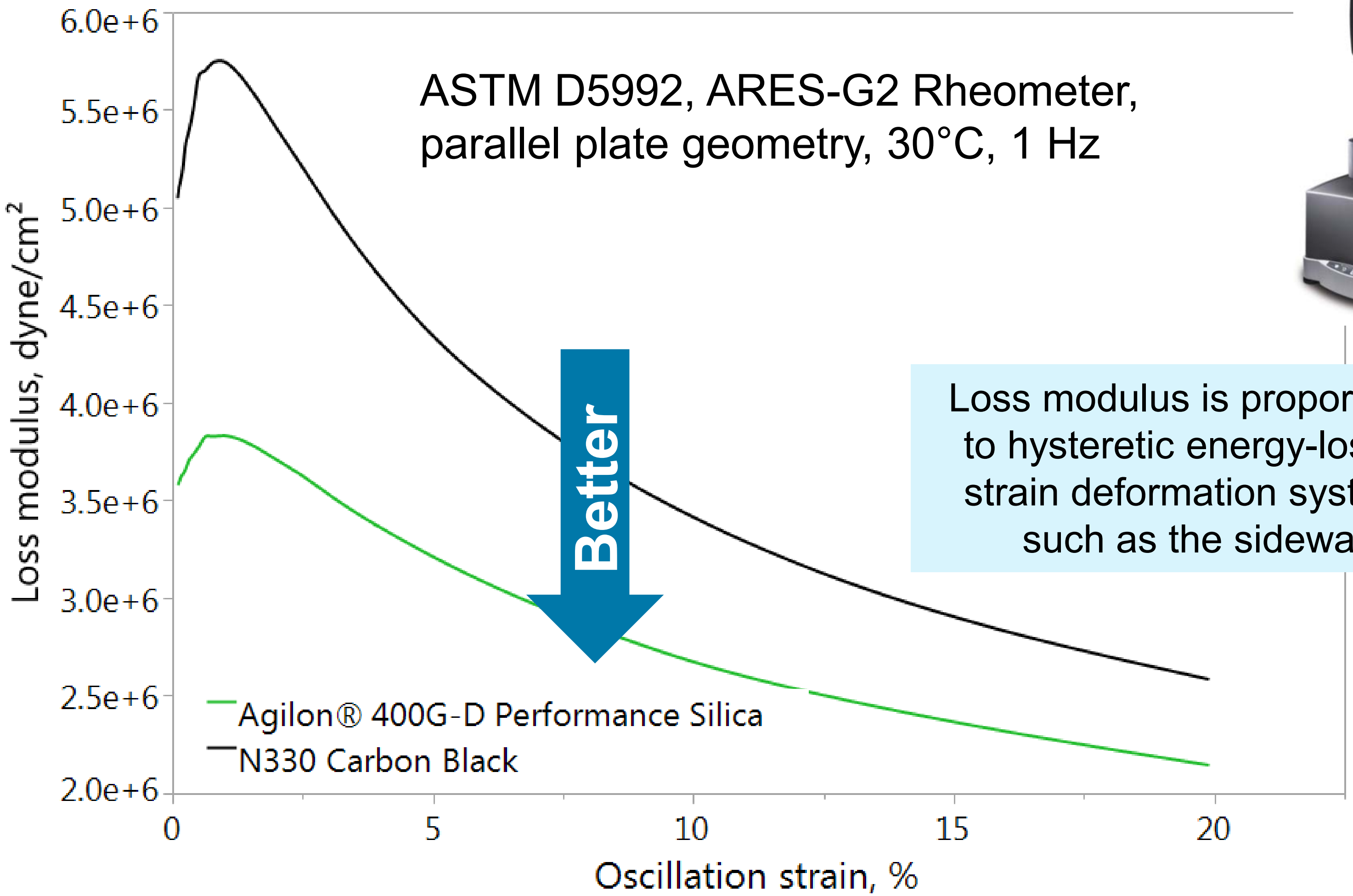
Technical Accomplishments – Energy Loss



30% reduction in energy loss as measured by tan δ at 60°C can translate to ≥ 1% increase in fuel efficiency

Technical Accomplishments – Energy Loss

ASTM D5992, ARES-G2 Rheometer, parallel plate geometry, 30°C, 1 Hz

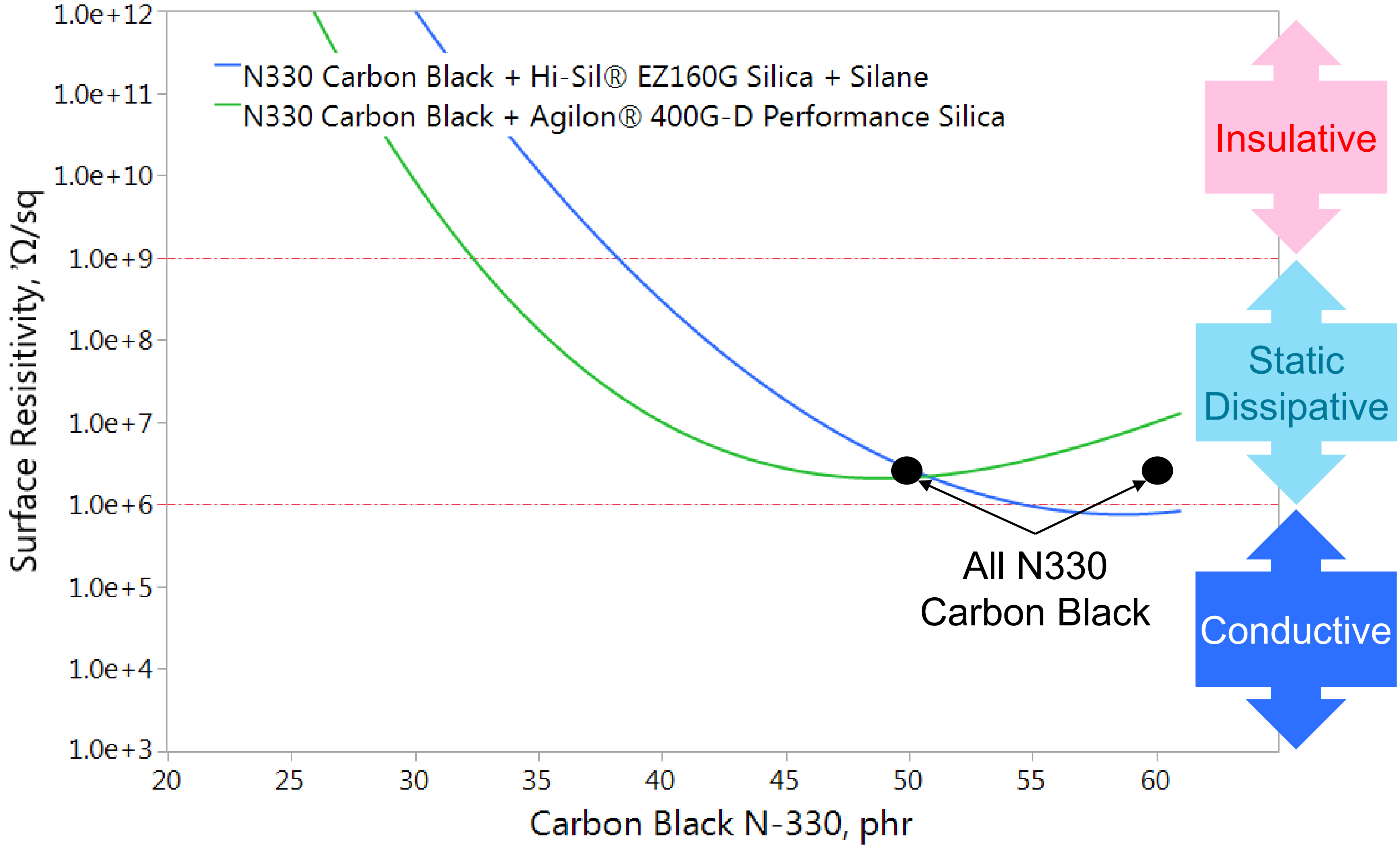


Loss modulus is proportional to hysteretic energy-loss of strain deformation systems such as the sidewall

Energy loss reduction giving better fuel efficiency confirmed by:

1. **Loss Modulus (shown above)**
2. **RPA Tan δ 100°C, 1.95% strain, 11 Hz**
3. **RPA Tan δ 100°C, 0.98% strain, 11 Hz**

Accomplishments – Electrical Surface Resistivity



Potential to go to lower carbon black level and higher Agilon level and still meet minimum static dissipation requirement

✓ **Increases potential to improve fuel efficiency**

Response to Previous Year Reviewer Comments

This project is a new start and was not reviewed last year

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

Remaining Challenges and Barriers

- Impact of reinforcing 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 trade-offs associated with commercial reinforcing systems
  - ✓ What is a statistically significant improvement in performance
  - ✓ 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 tradeoffs in commercial materials
- Synthesize silicas with varying surface chemistry
  - ✓ Identify tradeoffs with silicas with varying surface chemistry
- Synthesize silicas with varying morphology
  - ✓ Identify tradeoffs with silicas with varying morphology
- 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 delta improvement & ≤ 5% decrease in key performance properties
    - ➢ Prefer improved processing and resistance to degradative forces
- Accomplishments
  - ✓ Tests defined and in process of being verified
    - ➢ Qualitative and quantitative measurement of antidegradant migration / diffusion
    - ➢ Verified most test protocols with one Carbon Black, Hi-Sil, and Agilon Filler
  - ✓ Commercial fillers selected and testing in progress
    - ➢ Ability to meet fuel efficiency improvement promising
    - ➢ Agilon ability to at least partially address electrical surface resistivity promising
    - ➢ Awaiting results on other key performance properties
  - ✓ Other surface chemistries defined and synthesis 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

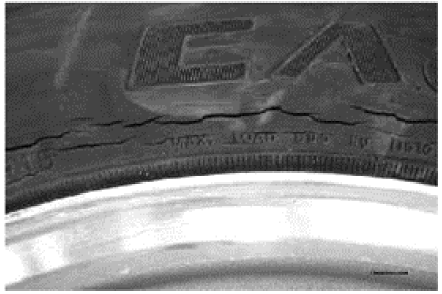
Typical Composition

- 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

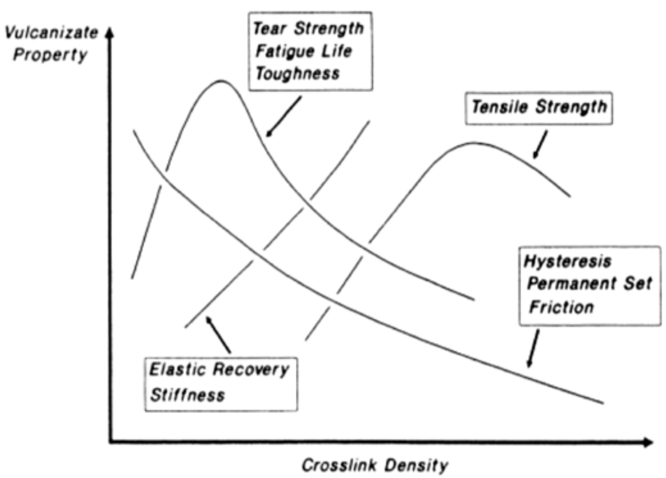
Sidewall Oxidative & Ozone Resistance

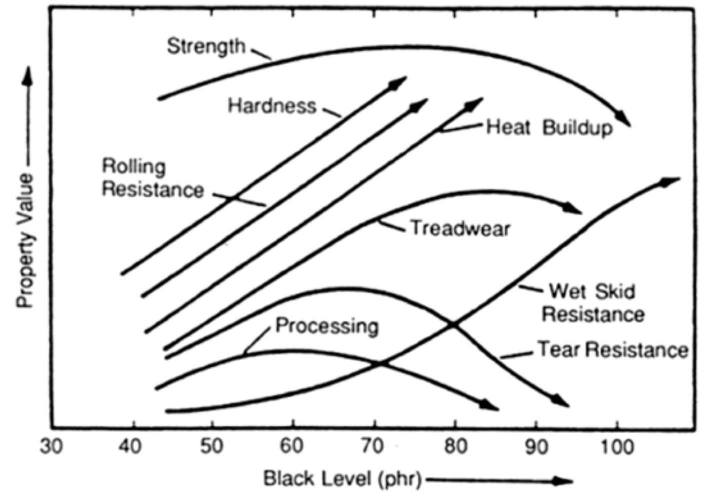


- **Key performance: resist oxidative (O_2) aging & ozone (O_3) attack**
- **Polymers with double bonds in their main chains (i.e. natural rubber and polybutadiene) susceptible to oxidation & ozonolysis**
  - ✓ Key sidewall polymers
- **Exposed surface cracks as material degrades & the chains break**
  - ✓ 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.