Paper 74

Sustainable Raw Material Review in NBR and HNBR

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ABSRACT

Sustainable Raw Material Review in NBR and HNBR

Many rubber and plastics manufacturers are looking to reduce their carbon footprints by adding recycled / sustainable alternatives to synthetic raw materials without sacrificing quality. Many advancements have been made in sustainable raw materials. However, most sustainable product literature and marketing is geared towards the tire industry due to its over- whelming size and research budgets. This paper looks at different sustainable options available to the rubber industry with a focus on NBR and HNBR applications and will discuss the pros and cons of each material.

Introduction

Most published sustainable raw material studies in polymers are done in tire formulations due to the overwhelming market size and research budgets enjoyed by most tire companies. The tire industry is by far the largest market sector in thermoset polymers and holds sales aspirations for most if not all raw material manufacturers. Sustainable raw material suppliers are no exception, and in fact, find favor with companies who sell directly to individual consumers as opposed to companies selling to corporations. Tire companies being suppliers to individual consumers are looking for ways to increase recycled / sustainable content in the hopes of swaying a sale in their favor due to an increase in public approval. Therefore, the tire companies embrace of recycled and sustainable products has created an explosion of studies aimed at sustainability in tire applications. Although informative, studies in tire formulations do not speak to oil and gas applications, or automotive under the hood applications. The goal of this paper is to present sustainability options: soybean oil, pyrolyzed rubber, and recycled silica in NBR and HNBR applications.

Soybean Oil Introduction

As the proverb says, necessity is the mother of invention, and this holds true for soybean oil use in tires. When the European Union restricted the use of aromatic oils with high levels of polyaromatic hydrocarbons (PAH's) it opened a door for alternative process oil sources. Unfortunately, both naphthenic oil and low polarity plasticizers are more expensive than aromatic oils and do not have the same degree of compatibility in tire formulations. Soybean oil has a variety of advantages including:

1). It is abundant and its renewable

2). It has similar thermal stability of other process oils.

3). It is chemically and physically compatible with common tire polymers.

4). It has no polyaromatic hydrocarbons (PAH's) so it is not a carcinogen.

In studies published by Goodyear soybean oil added at the mixer improved manufacturability and snow traction of tire formulations.(1) In base polymers extended with soybean oil manufacturability and wet traction of tire formulations were improved.(1)

Experiment I: Soybean Oil in an NBR Application

Soybean oil (SBO) was compared to dioctyl sebacate (DOS) in an NBR application and compared for rheology, unaged, and aged properties. The formulations mixed can be found in Table I.

Table I: NBR Formulations

	PHR	PHR
	Control	**SBO**
Nipol 1052	100.00	100.00
N650	75.00	75.00
Zinc Oxide	5.00	5.00
Stearic Acid	1.00	1.00
Naugard 445	2.00	2.00
DOS	10.00	
Soybean Oil (SBO)		10.00
Spider Sulfur	1.25	1.25
TBBS	1.00	1.00
TMTM	0.50	0.50
	195.75	195.75

Each batch was 2-pass mixed in a 1.6-liter BR Banbury and sheeted out and cooled on a two-roll mill. The mixing specification can be found in Table II.

Table II: NBR Hose Mixing Specification

First Pass Mix		**Second Pass Mix**	
0 Minutes	Add Nipol, 1/2 N650, stearic acid, Zinc oxide	0 Minutes	Sandwich batch and cure
90 Seconds	Add the rest	82.2°C	Sweep
126.6°C	Sweep	104.4°C	Drop
160.0°C	Drop		

Each batch was tested for the properties per the methods found in Table III.

Table III: Soybean Oil Compound Testing Protocol

Test	Method Used
MDR Rheology	ASTM D 5289
Unaged Physical Properties	ASTM D 412
Low Temperature Retraction	ASTM D 1329
Aged Physical Properties (70 hours @ 100°C)	ASTM D 573
Volume Swell (IRM901 and IRM 903)	ASTM D 471

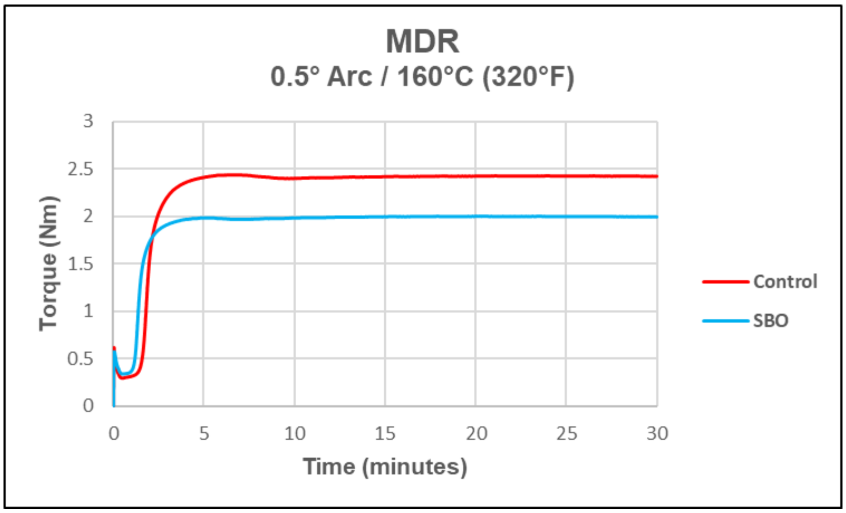
Experiment I: Results and Discussion

Each batch was evaluated for rheology properties at 160°C and the data can be found in Table IV and the rheology curves in Figure I.

Table IV: Rheology Properties ASTM D 5289

	Min Torque, ML, Nm	Cure Time, T50, min	Cure Time, T90, min	Scorch Time, TS1, min	Max Torque, MH, Nm
Control	0.29	1.91	3.04	1.47	2.44
SBO	0.34	1.42	2.36	1.14	2.00

Figure I: Rheology Curve ASTM D5289



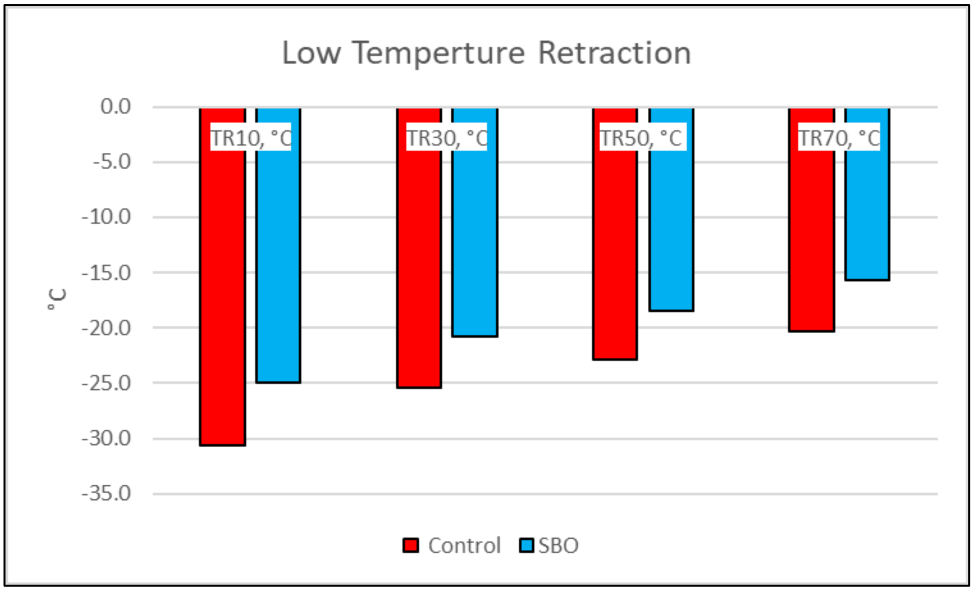
The soybean oil (SBO) has similar minimum torque as the Control and lower maximum torque values. The SBO has a faster scorch time and T90 cure time than the Control. Each batch was assessed for unaged physical properties and the data can be found in Table V.

Table V: Unaged Physical Properties ASTM D 412

	Control	SBO	Specification
Tensile, MPa	19.3	17.0	15.2 Min
50% Modulus, MPa	2.9	2.4	
100% Modulus, MPa	6.6	5.2	
200% Modulus, MPa	14.7	12.2	
300% Modulus, MPa	19.0	16.4	
Elongation, %	311	321	250% Min
Hardness, Shore A	76	76	75 +/- 5

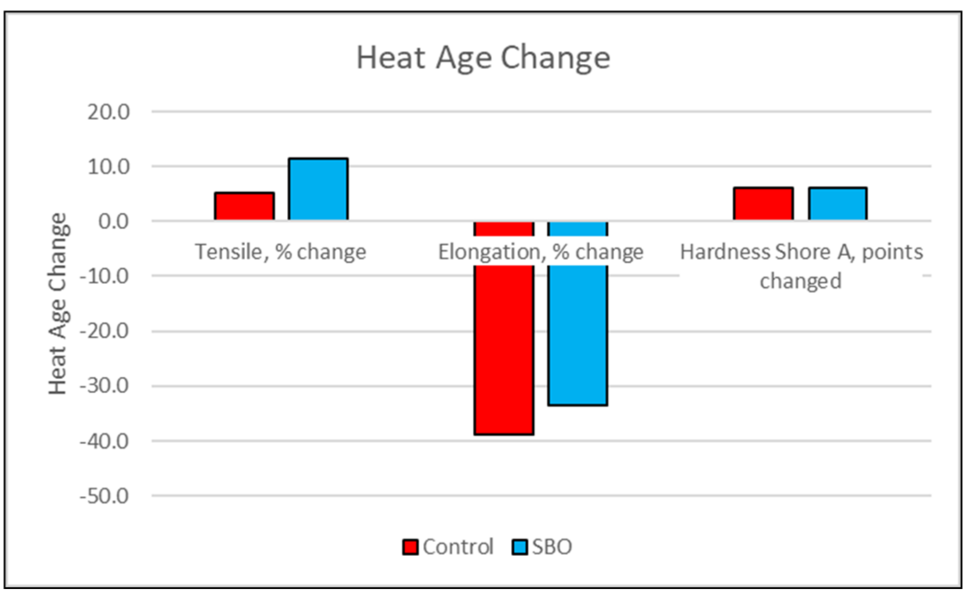
The SBO has slightly lower tensile and modulus properties when compared to the Control. The batches have similar elongation and hardness properties.
Each batch was evaluated for low temperature properties and the data can be found in Figure II.

Figure II: Low Temperature Retraction ASTM D 1329



The DOS has better low temperature properties than the soybean oil. To adjust for this a lower ACN NBR polymer would need to be used. Each batch was heat aged for 70 hours at 100°C and assessed and the data can be found in Figure III.

Figure III: Heat Aged Properties ASTM D 573



Both batches have a positive tensile change meaning the tensile properties increased after aging which is desirable. The SBO had less aged elongation change and similar hardness change as the DOS. Each batch was evaluated for fluid immersion properties in IRM 901 and IRM 903 and can be found in Figures IV and V.

Figure IV: Fluid Immersion IRM901

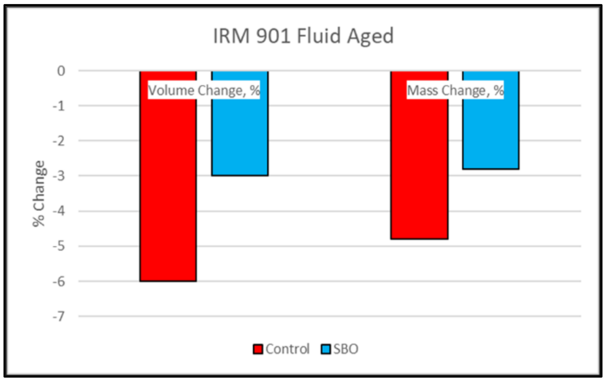
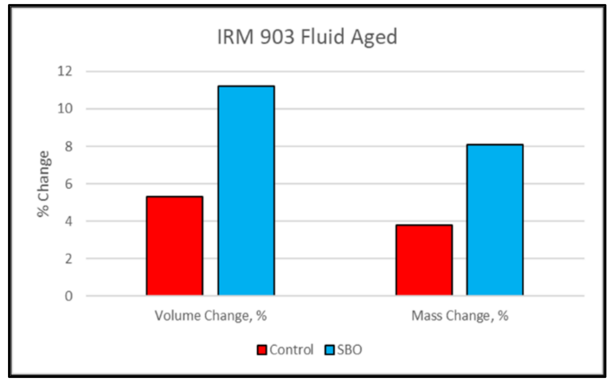


Figure V: Fluid Immersion IRM 903



The SBO has less volume and mass change in IRM 901 when compared to the DOS; however, it has more volume and mass change in IRM 903 oil.

The SBO in most instances performed similarly to the DOS compound. However, it had faster cure rate, less aged elongation change, and less change in IRM 901 oil. The DOS has slightly higher tensile and modulus, better low temperature properties, and better fluid aging in IRM 903.

Pyrolyzed Black Introduction

Increased environmental regulations have limited the amount of scrap tires allowed in landfills due to size, overwhelming numbers, resistance to deterioration, and heavy metal leaching. As the number of scrap tires over the last century increased a concerted effort was made to find ways to recycle scrap tires into a useable product. Scrap tires can be devulcanized, reclaimed, or ground. However, newer technology looks at pyrolyzing scrap tires to use as a replacement for carbon black. Pyrolyzed carbon black (RCB) derived from tires has a variety of advantages including:

1). Scrap tires are abundant.

2). Offers compounders a recycled product.

3). It is normally cheaper than virgin carbon black.

4). Requires less water to make and generates less air pollution [2]

In studies performed by Bolder Black Industries 100% pyrolyzed black has been found to perform similarly to a 600 or 700 series virgin carbon black. [3] In my experience from years of working with RCB it tends to decrease cure times and scorch safety so decreases in zinc oxide and stearic acid or a reduction in accelerators may be needed. A good pyrolyzed black can normally be used as a 30% replacement of virgin carbon black with little loss in physical properties.

Experiment II: Pyrolyzed Black in an NBR Extrusion Application

Pyrolyzed black was used as a 30% replacement of N650 and compared to 100% N650 in an NBR extrusion application and compared for rheology, unaged, and aged properties, tear resistance, dispersion, and Garvey die extrusion rating. The formulations mixed can be found in Table VI.

Table VI: NBR Formulations

	PHR	PHR
	Control	**RCB**
Nipol 1052	100.00	100.00
N650	75.00	52.50
Bolder Black (RCB)		22.50
Zinc Oxide	5.00	5.00
Stearic Acid	1.00	1.00
Naugard 445	2.00	2.00
DOS	10.00	10.00
Spider Sulfur	1.25	1.25
TBBS	1.00	1.00
TMTM	0.50	0.50
	195.75	195.75

Each batch was 2-pass mixed in a 1.6-liter BR Banbury and sheeted out and cooled on a two-roll mill. The mixing specification can be found in Table VII.

Table VII: NBR Hose Mixing Specification

First Pass Mix		Second Pass Mix	
0 Seconds	Add Nipol, 1/2 N650, stearic acid, zinc oxide	0 Seconds	Sandwich
90 Seconds	Add the Rest	93.3°C	Sweep
126.7°C	Sweep	104.4°C	Drop
148.9°C	Drop		

Each batch was tested for the properties per the methods found in Table VIII.

Table VIII: Pyrolyzed Black Compound Testing Protocol

Test	Method Used
MDR Rheology	ASTM D 5289
Unaged Physical Properties	ASTM D 412
Tear Resistance	ASTM D 624 Tear Die C
Dispersion Testing	ASTM D 7723
Garvey Die Extrusion Rating	ASTM D 2230

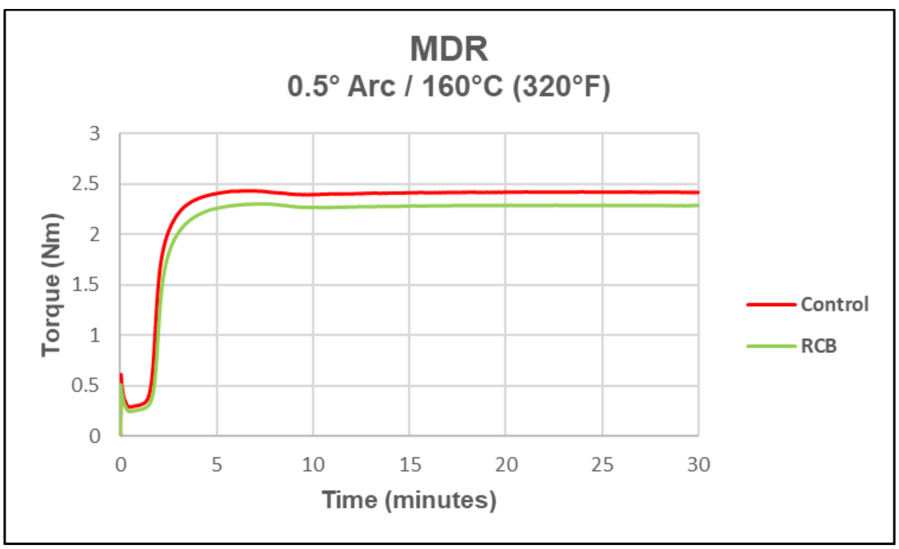
Experiment II: Results and Discussion

Each batch was evaluated for rheology properties at 160°C and the data can be found in Table IX and the rheology curves in Figure VI.

Table IX: Rheology Properties ASTM D 5289

	Min Torque, ML, Nm	Cure Time, T50, min	Cure Time, T90, min	Scorch Time, TS1, min	Max Torque, MH, Nm
Control	0.29	1.91	3.04	1.47	2.44
RCB	0.25	2.05	3.34	1.60	2.31

Figure VI: Rheology Curve ASTM D5289



The RCB has similar cure properties as the Control N650 batch. This is interesting because in most polymers a decrease in cure time and scorch safety are common and we did not see this in

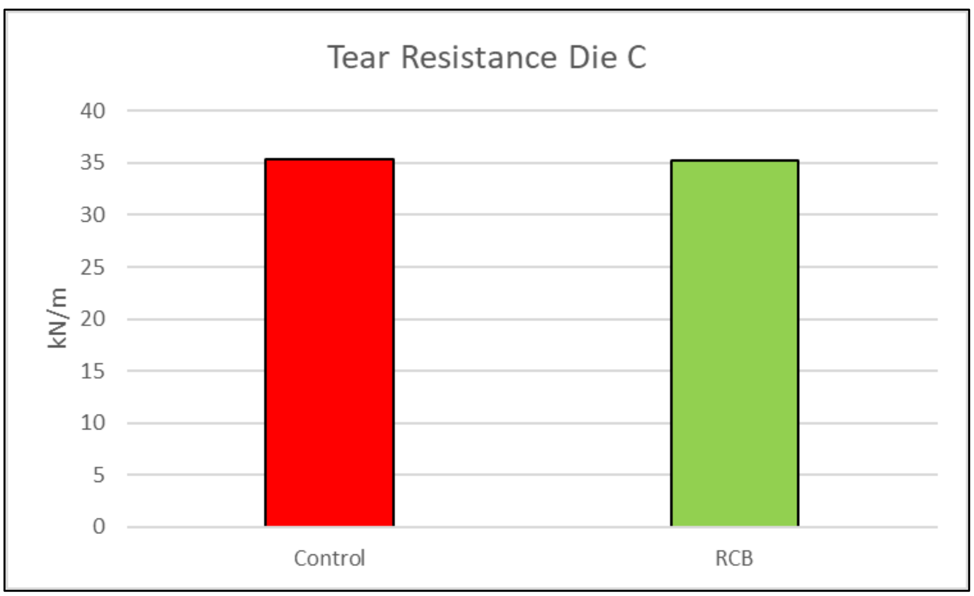
NBR. Each batch was assessed for unaged physical properties and the data can be found in Table X.

Table X: Unaged Physical Properties ASTM D 412

	Control	RCB	Specification
Tensile, MPa	19.3	18.2	15.2 Min
50% Modulus, MPa	2.9	2.5	
100% Modulus, MPa	6.6	5.4	
200% Modulus, MPa	14.7	12.7	
300% Modulus, MPa	19.0	17.7	
Elongation, %	311	313	250% Min
Hardness, Shore A	76	74	75 +/- 5

The RCB has similar tensile, elongation, and hardness properties as the Control N650. However, the RCB does have lower modulus properties. Each batch was evaluated for tear resistance and the data can be found in Figure VII.

Figure VII: Tear Die C Properties ASTM D 624



Both batches have similar tear resistance properties. Both batches were assessed for dispersion using a dispergrader and the % dispersibility and the X and Y data can be found in Figures VIII and IX.

Figure VIII: % Dispersibility ASTM D 7723

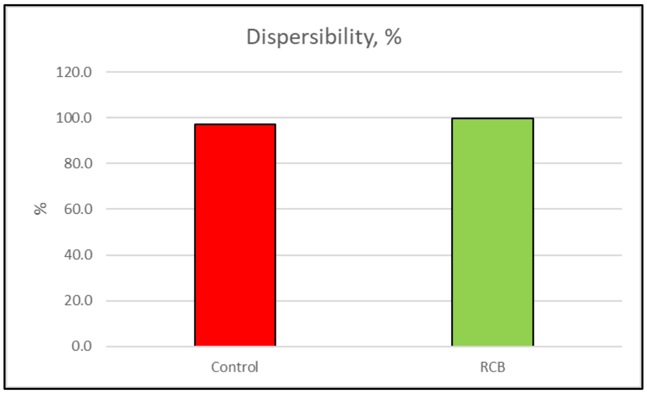
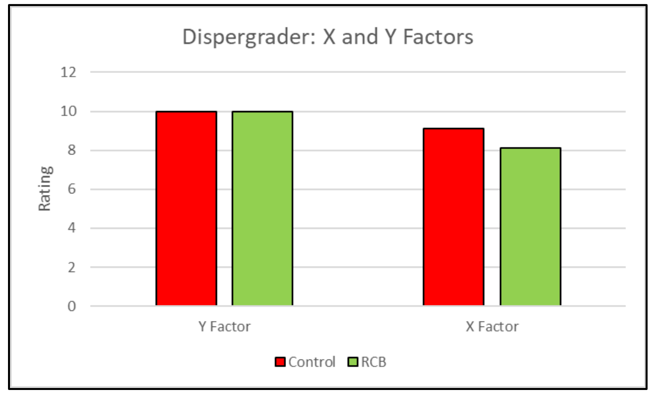


Figure IX: Dispersion X & Y Factors



Both compounds show excellent % dispersion with both compounds around 100%. The Y factor is a rating based on large agglomerate count and both batches have similar ratings. The X factor is akin to Phillips Dispersion and gives a number from 1 to 10 with ten being the best dispersion and one being the worst. The N650 had an X rating of nine and the RCB had an X rating of eight. Each batch was compared for Garvey die extrusion rating and the results can be found in Pictures I and II.

Picture I: Control Garvey Die

Picture 2: RCB Garvey Die

Both batches had excellent Garvey die extrusion ratings.

In most instances the 30% replacement of N650 carbon black with RCB pyrolyzed black performed similarly to the 100% N650 compound. It had similar rheology properties, tensile, elongation, durometer, tear resistance, and dispersibility. However, it did have lower modulus values.

Introduction Recycled Silica

The demand for silica in the rubber industry has skyrocketed with the push for low rolling resistance tires to improve fuel economy. Unlike carbon black, which is standardized regardless of manufacturer by ASTM D 1765, silica has no standardization system. This means that many silicas produced have no off-set so if a manufacturer goes out of business or if a line or plant goes down there is no identical drop-in. Therefore, changes in silica manufacturer will require some formulation adjustments which makes companies more open to evaluation of new products. I remember early in my career evaluating silica that came from ground automotive windshields. Although interesting, it was more expensive than the current precipitated silica in the market. Since then, silica pyrolyzed from rice hulls has been introduced. In his study Narendra Singh Chundawat found that rice hull silica had similar particle size distribution as conventional silica and that up to a 50% replacement of conventional silica with rice hull silica yielded no change in physical properties.(4) One of the draw backs of rice hull silica is that it tends to be gray in color which eliminates its use as a replacement for precipitated silica in colored goods. Recycled silica has also been introduced that is made from steel mill waste. Silica produced from steel mill waste is amorphous and considered non-carcinogenic like standard precipitated silica. Recycled silica has a variety of advantages including:

1). Offers compounders a recycled product.

2). It comes from abundant low-cost feed stocks (5)

3). Its 99% pure silica (5)

4). Produces no toxic or hazardous waste (5)

5). Requires less energy and produces lower emissions than conventional silica (5)

Experiment III: Recycled Silica in an HNBR Formulation

Recycled silica was used as a 100% replacement for Ultrasil 7000 in an HNBR formulation and compared for rheology, unaged properties, tear resistance, specific gravity, and abrasion resistance. The formulations mixed can be found in Table XI.

Table XI: HNBR Formulations

	PHR	PHR
	Control	RHS
Zetpol 2020EP	100.00	100.00
N330	20.00	20.00
Ultrasil 7000	30.00	
DOS	8.00	8.00
Zinc Oxide	5.00	5.00
Silquest A 174	1.50	1.50
TMQ	1.00	1.00
YAVA 1124 PPI (RS)		30.00
DBPH-50	10.00	10.00
Tac 72%	2.00	2.00
	177.50	177.50

Each batch was 2-pass mixed in a 1.6-liter BR Banbury and sheeted out and cooled on a two-roll mill. The mixing specification can be found in Table XII.

Table XII: HNBR Mixing Specification

First Pass Mix		Second Pass Mix	
0 Seconds	Add Zetpol, N330	0 Seconds	Sandwich
60 Seconds	Add Ultrasil or Yava 1124 and Silquest, DOS	93.3°C	Sweep
120 Seconds	Add the Rest	104.4°C	Drop
126.7°C	Sweep		
137.8°C	Drop		

Each batch was tested for the properties per the methods found in Table XIII.

Table XIII: NBR Hose Testing Protocol

Test	Method Used
MDR Rheology	ASTM D 5289
Unaged Physical Properties	ASTM D 412
Tear Resistance	ASTM D 624 Tear Die C
Specific Gravity	ASTM D 792
Rotary Drum Abrasion	ASTM D 5963

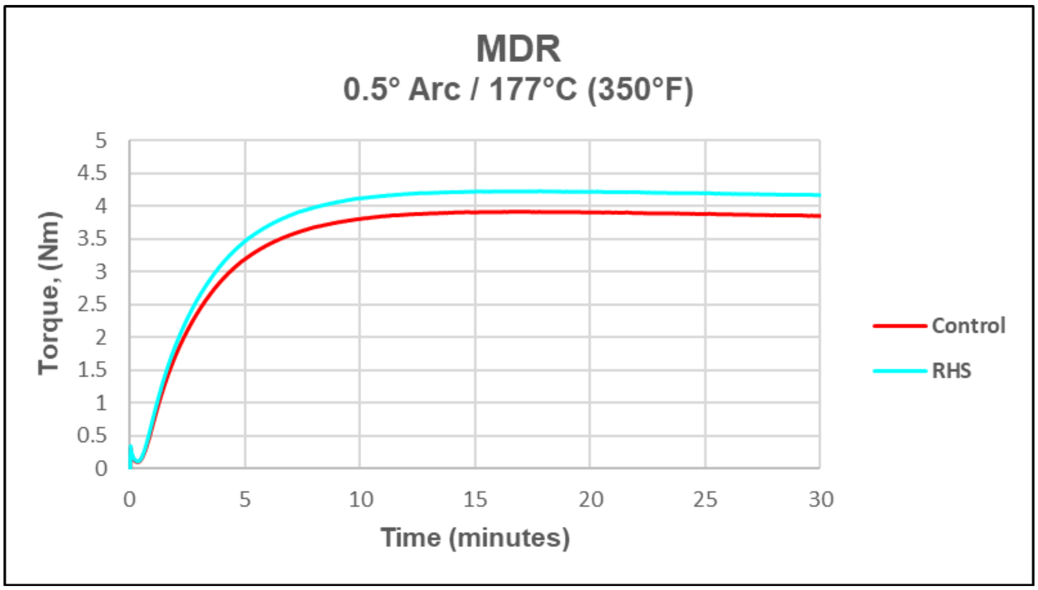
Experiment III: Results and Discussion

Each batch was evaluated for rheology properties at 176.6°C and the data can be found in Table IX and the rheology curves in Figure X.

Table XIV: Rheology Properties ASTM D 5289

	Min Torque, ML, Nm	Cure Time, T50, min	Cure Time, T90, min	Scorch Time, TS1, min	Max Torque, MH, Nm
Control	0.10	2.34	6.74	0.58	3.92
RS	0.11	2.32	6.64	0.56	4.23

Figure X: Rheology Curve ASTM D5289



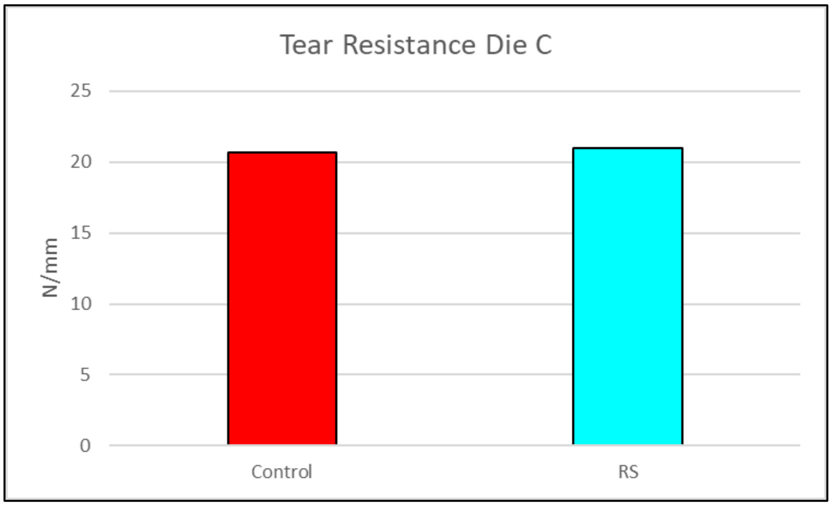
The recycled silica has a similar rheology curve as the Control with just a slightly higher maximum torque value. Each batch was assessed for unaged physicals and the data can be found in Table XV.

Table XV: Unaged Physical Properties ASTM D 412

	Control	RS
Tensile, MPa	17	16.6
50% Modulus, MPa	3.53	4.27
100% Modulus, MPa	9.51	11.3
Elongation, %	143	127
Durometer, points	81	81

The recycled silica has similar tensile and hardness properties as the Ultrasil 7000. The recycled silica has a higher modulus and lower elongation properties than the Ultrasil 7000. Both batches were evaluated for tear resistance and the data can be found in Figure XI

Figure XI: Tear Die C Properties ASTM D 624



Both batches have similar tear resistance properties. Each batch was assessed for specific gravity and the data can be found in Table XVI.

Table XVI: Specific Gravity

	Control	RS
Specific Gravity	1.177	1.177

Both batches have the same specific gravity. Each batch was evaluated for rotary drum abrasion resistance and the data can be found in Figure XVI.

Figure XII: Abrasion Resistance

The Ultrasil 7000 has slightly less abrasion loss than the recycled silica.

The recycled silica has similar rheology properties, tensile, hardness, specific gravity, and tear resistance as the Ultrasil 7000. The Recycled silica also had higher modulus and maximum torque values meaning it was stiffer which may have attributed to its slightly higher abrasion loss.

Conclusion

Many rubber and plastics manufacturers are looking to reduce their carbon footprint by adding recycled / sustainable alternatives to synthetic raw materials without sacrificing quality. Many advancements have been made in sustainable raw materials; however, most published studies involving sustainable / recycled materials are done in tire applications. However informative, these tire studies do not speak to the rubber market as a whole. The goal of this paper was to evaluate soybean oil, pyrolyzed tire RCB, and recycled silica in NBR and HNBR applications. Soybean oil performed similarly to DOS in most instances. However, it had faster cure rate, less aged elongation change, and less change in IRM 901 oil. The DOS Control has slightly higher tensile and modulus, better low temperature properties, and better fluid aging in IRM 903. The 30% replacement of N650 with pyrolyzed tire (RCB), in most instances performed similarly to the 100% N650 compound. It had similar rheology properties, tensile, elongation, durometer, tear resistance, Garvey die extrusion rating, and dispersibility. However, it did have lower modulus values. The recycled silica had similar rheology properties, tensile, hardness, specific gravity, and tear resistance as the Control Ultrasil 7000. The Recycled silica also had higher modulus and maximum torque values meaning that it was stiffer which may have attributed to its slightly higher abrasion loss.

Bibliography

1). **Soybean Oil as a Replacement for Petroleum-Based Oils in Tire Tread Compounds Lauren Brace*,** The Goodyear Tire & Rubber Company (Akron, OH, USA) Bob Woloszynek, The Goodyear Tire & Rubber Company (Akron, OH, USA

2). https://www.bolderindustries.com/

3). New Sustainable Tire Inner Liner Using Bolder Black
Mike Kumbalek and Michael Jacobsson – Bolder Industries

4). **Rice Husk Silica as a Sustainable Filler in the Tire Industry**: Narendra Singh Chundawat a, Bhavani Shanker Parmar a,b, Arup Saha Deuri b,Dilip Vaidya b, Sapana Jadoun c, Payam Zarrintaj d, Mahmood Barani e,*,Narendra Pal Singh Chauhan

5). https://yavasilica.com/product/