Carbonized Soybean Hull as a Replacement for Carbon Black in Tire Sidewalls

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ABSTRACT

Carbon black is the predominant filler in the rubber market because it has superior reinforcement, has lower specific gravity than most mineral fillers, and has excellent dispersion due to high surface activity. Carbon black is plagued by many problems, such as, being derived from fossil fuels, being a carcinogen, being an atmospheric pollutant, and market volatility because the price of carbon black is indexed to the price of oil. Many companies are looking for sustainable or recycled fillers that can replace carbon black. Soybean hull has the potential to be a cost effective and sustainable filler that does not impact the human food supply and would add income to soybean farmers. This paper evaluates the ability of soybean hulls to replace a 700 series carbon black in a tire sidewall formulation.

Introduction

Carbon black is the predominant filler in the rubber market because it has superior reinforcement, has lower specific gravity than most mineral fillers, and has excellent dispersion due to high surface activity. Carbon black by definition is an engineered product that is derived from the combustion of hydrocarbon oil. Since the feedstock comes from oil, the price of carbon black is indexed to the cost of oil, which has led to market volatility in recent years. Carbon black is considered a carcinogen because it has polyaromatic hydrocarbons (PAH's) on its surface. The manufacture of carbon black contributes to air pollution in the form of NOx and SOx, and it's allowable emissions are regulated by the EPA. Due to these many challenges facing the carbon black industry many manufacturers are looking for sustainable filler alternatives with similar reinforcement and processability.

Soybean hulls are the plant scraps left over after the soybean has been harvested and are normally discarded to landfills or used as a filler in low-cost animal feed. Therefore, the use of soy hulls in industrial applications does not impact the human food supply like other sustainable options. It also stops the hull from going to landfill where it generates methane as it decomposes, and it would provide extra income for soybean farmers. In June of 2023 the cost of carbon black is $1,960 / metric ton and the cost of soy hulls is $165 / metric ton.[1, 2]

The companies most interested in pursuing sustainable raw materials are ones that sell to the average consumer like automotive and tire companies, shoe companies, sporting goods manufacturers, roofing companies, and flooring companies. Companies marketing to the average consumer are hoping that adding sustainable or recycled content will give them an edge over the competition since many individuals are looking for ways they can reduce environmental concerns regarding fossil fuels. These companies are looking for good sustainable or recycled alternatives to synthetic raw materials to improve marketability.

In a previous paper, the concept of carbonized soybean hull (CSH) was explored and found to be successful as a 25% replacement of N550 in a generic NR formulation that was open mill mixed with no addition of oil.[3] In this paper, we evaluate CSH as a partial replacement for a 700 series carbon black in a model sidewall tire formulation.

Experiment

The soybean hull was ground in a high-speed grinder and pyrolyzed for 3 hours at 350°C in a nitrogen gas atmosphere under vacuum in a metal fixture. After cooling, the CSH was ground again and rinsed in toluene for one hour to remove any residual oil, filtered, and dried for 72 hours. The CSH was tested for carbon black properties DBP Absorption ASTM D 2414, pH ASTM D 1512, Carbon Black Typing ASTM D 3849, Density ASTM D 297, modified sieve residue, and Nitrogen Adsorption ASTM D 6556. The sample was mixed into a model sidewall tire formulation and evaluated against N774 for MDR Rheology ASTM D 5289, Unaged Physical Properties ASTM D 412, Hardness Properties ASTM D 2240, Specific Gravity ASTM D 792, Dispergrader ASTM D 7723. and Tear Die C ASTM D 624.

Experiment 1: Discussion & Results

Pictures of the soybean hull pellets, ground soybean hulls, and the carbonized CSH can be found in Figures I through VI.

Figure I: Soybean Hull

Figure II: Ground Soy Hull

Figure III: Carbonized CSH

Figure IV: CSH in Toluene Bath

Figure V: Dried CSH

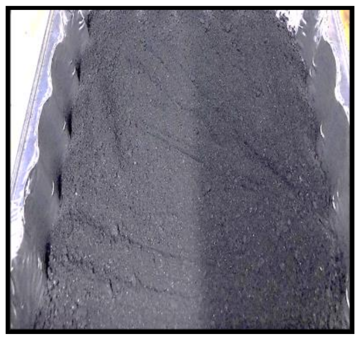


Figure VI: Extracted Material

During the carbonizing and rinsing process the soybean hulls lost 60% of their mass.

The CSH was tested for ASTM D 2414 DBP Absorption and the data can be found in Table I.

Table I: DBP Absorption

	N774	CSH
DBP Absorption cm^3/100g	73.0	23.2

DBP Absorption is a test used to characterize the structure of a carbon black. The more complex the geometry of the agglomerate, the higher the structure. Structure is related to processing and higher structure carbon blacks tend to have better dispersion. The N774 has a much higher structure than the CSH. In fact, the CSH has a lower structure than N990 thermal black.

The CSH was tested for ASTM D 3849 Carbon Black Typing and this test determined that the CSH does not have the same aggregate / agglomerate structure of standard carbon black morphology that resembles a cluster of grapes. The CSH was blocky and flat and had more of a platy aspect ratio reminiscent of a clay or a talc mineral filler. Since the structure of the CSH was so different, a particle size could not be determined. Examples of normal carbon black morphology and the CSH morphology can be found in Figures VII and VIII

Figure VII: Carbon Black Morphology

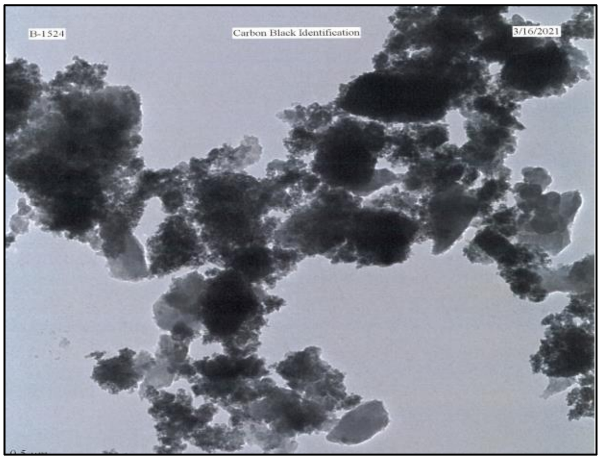
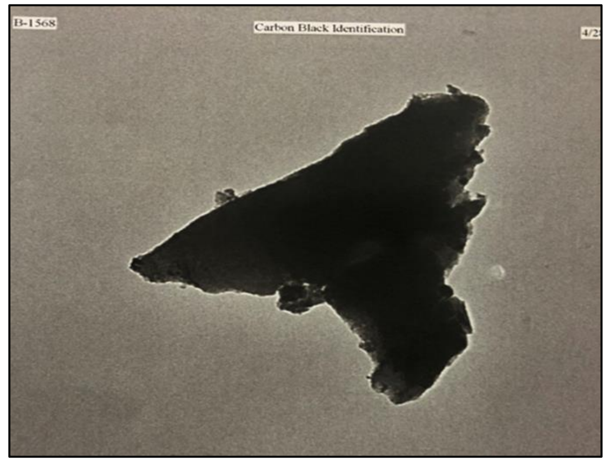


Figure VIII: CSH Morphology



The CSH was tested for Nitrogen Adsorption ASTM D 6556 to determine surface area and no surface area number could be determined through this test. The CSH was tested for pH ASTM D 1512 and the data can be found in Table II.

Table II: Carbon Black pH

	CSH	Carbon Black
pH	**9.04**	**8.0-12.0**

The pH of a filler can indicate what effect it will have on cure properties. The more acidic the filler the slower they cure and the faster they scorch. The CSH has a similar pH as carbon black.

The CSH was tested for density and the data can be found in Table III.

Table III: Density

	CSH	Carbon Black
Density	1.21	1.80

The density of the CSH is much lower than carbon black. In fact, it is even lower than coal dust which is used because of its low gravity to reduce weight and lb. volume cost. This means if successful, that CSH could be a low specific gravity filler that could be used to reduce the weight of rubber articles in a sidewall application to improve fuel economy.

A modified sieve residue test was done on the CSH to see how much material would pass through an 80M, 100M, and 325M screen and the data can be found in Table IV.

Table IV: Modified Sieve Residue

	% Through 80M	% Through 100M	% Through 325M
280 Seconds	91%	83%	44%

Typical rubber fillers should have 95% or more pass through a 325M screen. This shows that the grinding process for the CSH needs to be refined more.

The CSH was used as a 25% replacement for N774 and mixed into a model tire sidewall formulation and the formulation can be found in Table V.

Table V: Sidewall Formulation

	PHR	PHR
	Control	25 CSH
Natural Rubber	50.00	50.00
Polybutadiene Rubber	50.00	50.00
Carbon Black, N774	55.00	41.25
CSH		13.75
Activation System	5.00	5.00
Antioxidant System	6.00	6.00
Cure System	3.00	3.00
	169.00	169.00

Both batches were 2-pass mixed in a 1.6-liter BR Banbury and sheeted out and cooled on a two-roll mill.

The mixing data can be found in Table VI and Figures IX through XII.

Table VI: Mixing Data

Batch	Time (min)	Temperature (°C)	Integrated Power (HP*min)
1st Pass Mixing			
N774 Control	8.48	148.22	118.03
N774 / CSH (75:25)	7.00	148.66	93.93
Final Pass Mixing			
N774 Control	2.35	103.74	31.35
N774 / CSH (75:25)	2.35	104.47	34.36

Figure IX: 1st Pass Temperature

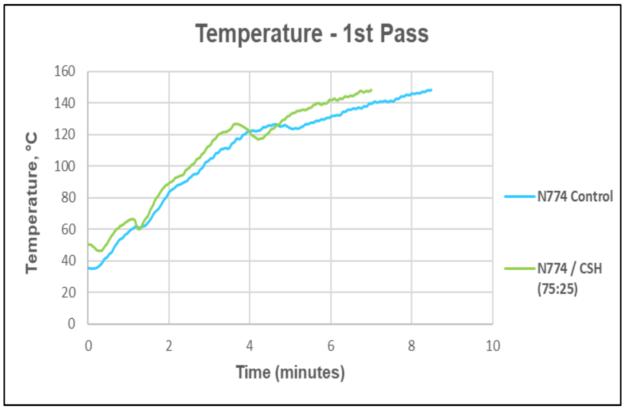


Figure X: 2nd Pass Temperature

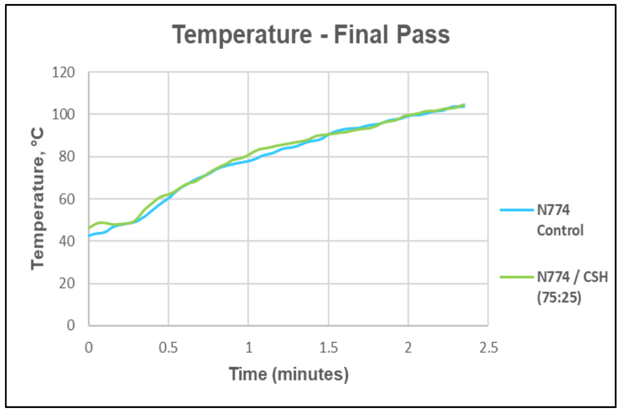


Figure XI: 1st Pass Integrated Power

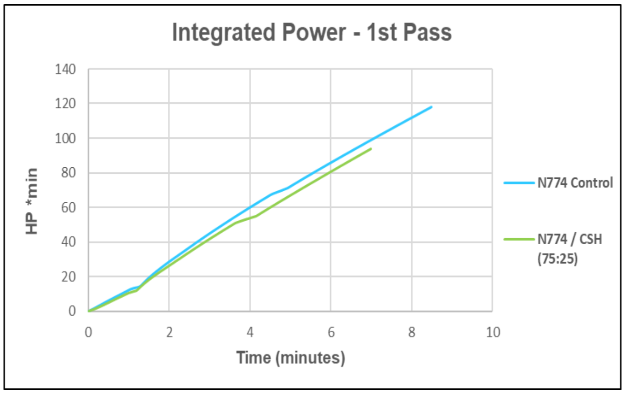
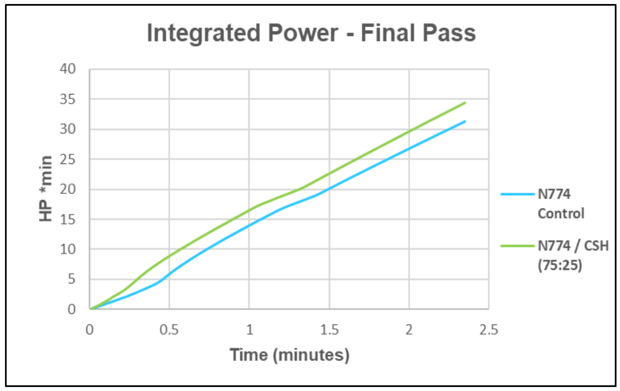


Figure XII: 2nd Pass Integrated Power



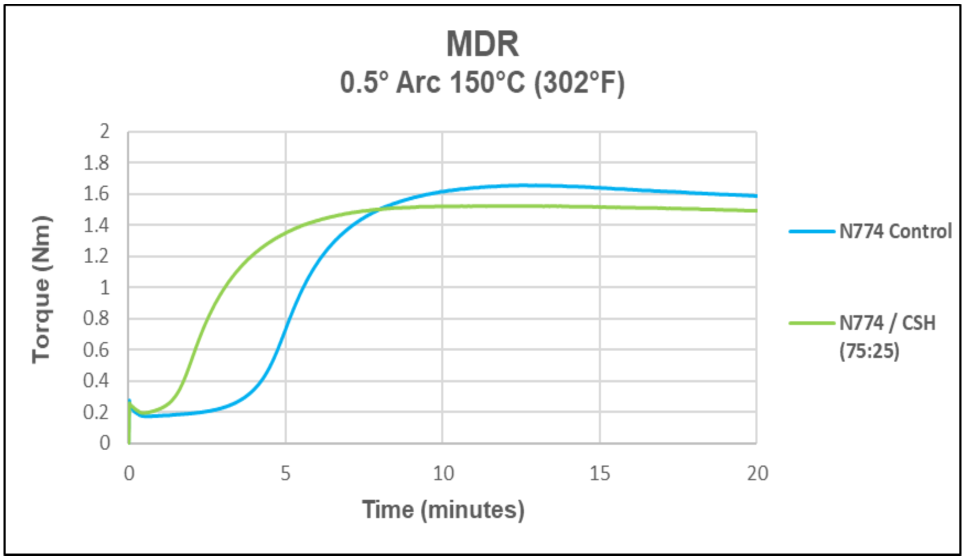
The N774 and the N774 with the partial replacement of CSH mixed very similarly.

Each batch was tested for MDR Rheology ASTM D 5289 and the data can be found in Table VII and Figure XIII.

Table VII: MDR Rheology Data

	Min Torque, ML, Nm	Cure Time, T50, min	Cure Time, T90, min	Scorch Time, TS1, min	Max Torque, MH, Nm
N774 Control	0.17	5.35	8.03	3.51	1.66
N774 / CSH (75:25)	0.19	2.65	5.43	1.46	1.52

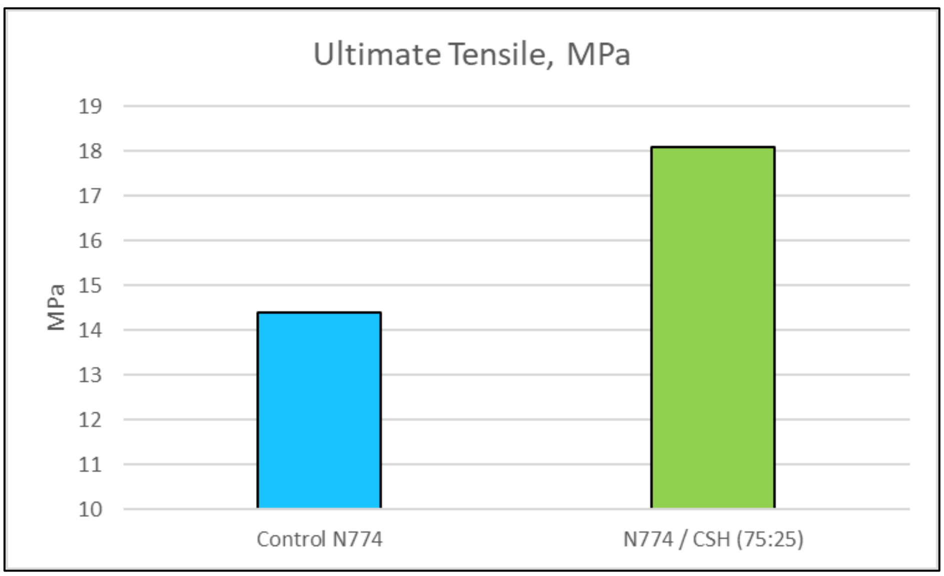
Figure XIII: MDR Rheology Curve



Even though the CSH has a similar pH as carbon black it still decreases the scorch and T90 cure times. However, it has similar minimum torque, meaning it will have similar viscosity properties as N774. It also has similar maximum torque properties, signifying similar stiffness and or crosslink density.

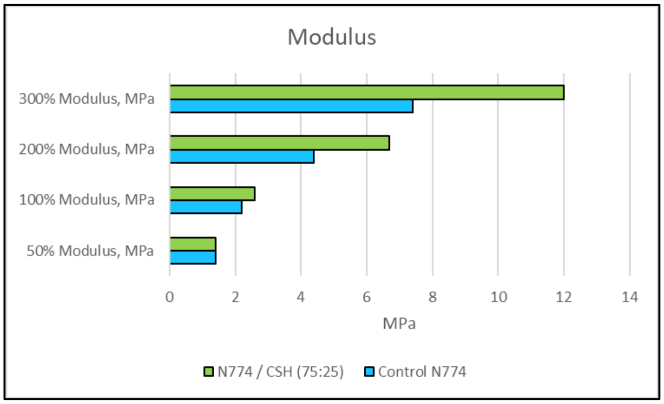
Test specimens were molded for each compound T90 + 2 minutes at 150°C and tested for unaged physical properties ASTM D 412 and the data can be found in Figures XIV through XVII

Figure XIV: Tensile Properties



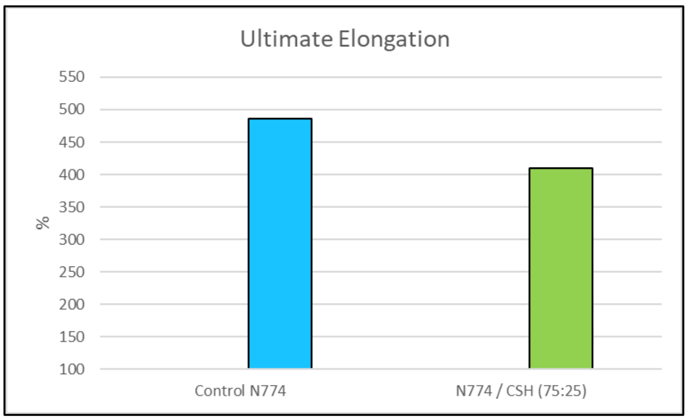
The replacement of N774 with 25% CSH increased tensile properties considerably.

Figure XV: Modulus Properties



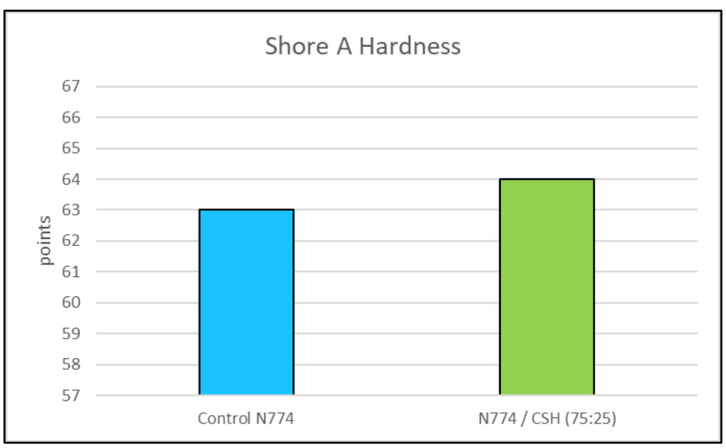
The addition of CSH increased the modulus properties at higher elongations and had similar modulus properties as the N774 at lower elongations.

Figure XVI: Elongation Properties



The addition of CSH decreased the elongation properties which is not surprising since it increased the modulus.

Figure XVII: Hardness Properties



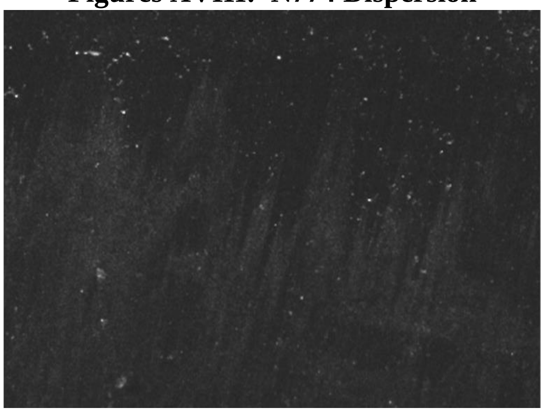
Both compounds have similar hardness / durometer properties which is interesting because the CSH had higher modulus.

Each batch was tested for dispersion properties and the data can be found in Table VIII and Figures XVIII and XIX.

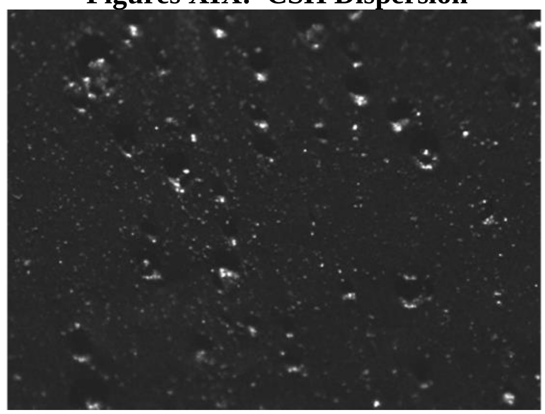
Table VIII: Dispergrader Results

	X	Y	Z	White Area, %	Dispersion %	Avg. Agg. Size (um)	Agg. Size Std. Dev. (um)
Control N774	7.68	9.81	90.69	3.26	**83.70**	8.44	5.40
CSH	3.88	8.66	78.89	7.39	**63.06**	13.63	8.31

Figures XVIII: N774 Dispersion



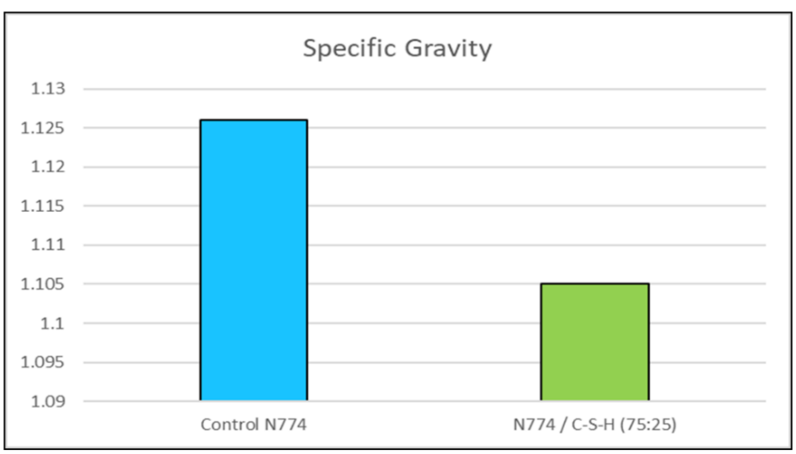
Figures XIX: CSH Dispersion



The dispergrader results show that the CSH has 25% worse dispersion than the N774 and a larger agglomerate size which is not surprising since the CSH is not pelletized. The dispersion results make the higher tensile results of the CSH more remarkable.

Both batches were tested for specific gravity properties and the data can be found in Figure XX.

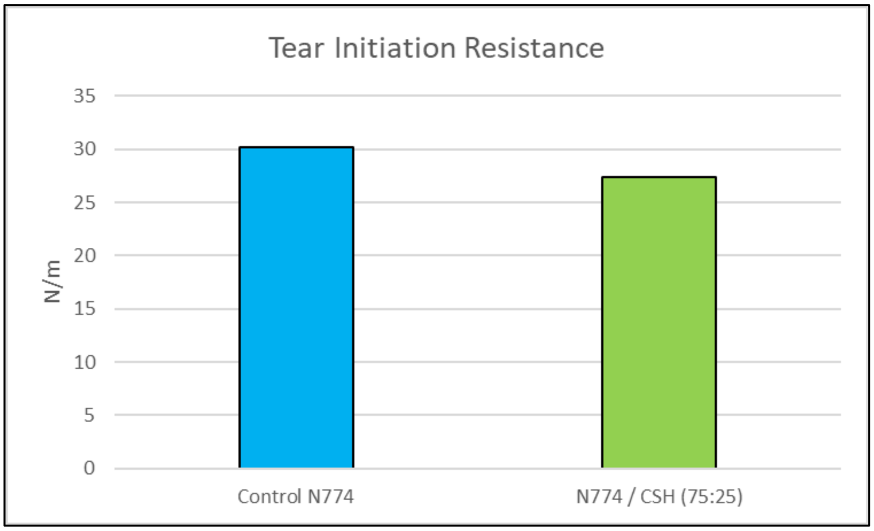
Figure XX: Specific Gravity



A 25% replacement of N774 with CSH reduced the specific gravity 2% effectively reducing the weight of a tire to improve fuel economy.

Each batch was tested for tear initiation resistance and the data can be found in Figure XXI.

Table XXI: Tear Die C Resistance



The addition of CSH reduced the tear initiation properties slightly.

Conclusion

The CSH showed promise as a sustainable alternative to carbon black by increasing tensile and modulus properties while reducing the compound specific gravity, effectively reducing the weight of the tire and improving automotive fuel economy. The grinding process needs to be refined and the carbonization temperature may need to be increased to improve dispersion properties and tear resistance. Pelletization would also improve dispersion and handling. The scorch safety issues could be overcome by changing the compound cure system or by possibly adding surfactants during pelletization. With minor modifications CSH could be a viable alternative to carbon black in any rubber application looking to increase sustainability, reduce product weight, or improve lb. volume cost.

Bibliography

1). Carbon Black Prices, News, Monitor, Analysis & Demand (chemanalyst.com)

2). agnr.osu.edu/sites/agnr/files/imce/pdfs/Beef/SoybeanHulls.pdf

3). Carbonized Soybean Hull as a Sustainable Filler in Rubber Products: Rubber News, June 26th, 2023 pgs. 13-16.