**Paper**

# Carbonized Soybean Hull as a Sustainable Filler in Rubber Products

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## ABSTRACT

Many rubber manufacturers are looking for sustainable alternatives to synthetic filler products derived from fossil fuels. Carbon black owns the lion's share of the filler market but is plagued by costs that are indexed to the price of oil, EPA regulations, and status as a carcinogen. Unfortunately, most mineral fillers have inferior properties, are hard to process, and have higher specific gravities that increase the weight of the end rubber product. Soybean hull has the potential to be a cost effective and sustainable alternative filler that does not impact the food supply. This paper evaluates the ability of soybean hull to be ground, carbonized in a nitrogen atmosphere, and used as a partial replacement for carbon black.

## Introduction

Many industries are looking for sustainable alternatives to synthetic filler products that stem from fossil fuels. Currently, carbon black enjoys the lion's share of filler usage in the world. It has excellent reinforcing properties, provides UV protection, and is easier to process than other types of fillers. Unfortunately, the cost of carbon black is indexed to the price of oil so natural disasters, oil shortages, and political strife can cause economic swings that can be detrimental to the rubber industry. Carbon black is also governed by EPA regulations restricting NOx and SOx emissions that dictate how many emissions each plant is allowed to produce, which in recent history, shuttered some plants for months at a time creating supply issues. Carbon black is produced from oil that has polyaromatic hydrocarbons (PAH's) on its surface which makes it a carcinogen, increasing the likelihood of further regulations down the road. Many rubber manufacturers are looking for sustainable filler options that do not carry health risks. If carbonizing soybean hulls in a nitrogen atmosphere is successful, this could lead to a new sustainable filler that could compete with carbon black and increase the need for soybean farm production in North America without impacting the food supply since the soybean hull is what is left over after the soybean has been harvested.

Currently, many companies have successfully pyrolyzed carbon black from used tires and are currently selling this recycled black to the market. However, the reinforcing properties of pyrolyzed black are low which limits where and how it can be used. Recently, it has come to light that salmon die-off in the western United States may be attributed to common tire tread antioxidants / antiozonants TMQ and 6PPD. If these antidegradents see future regulations, this may dramatically limit the pool of tires available for recycle.

Work has been done in Japan at the Tsuruoka National College of Technology to use carbonized soybean hulls to increase the conductivity in rubber compounds. The paper is called *"Electromagnetic Shielding in Rubber Composite Materials with Soy Hull Carbon Particles"*.

## Experiment I

100% soybean hull was weighed to 50 grams and samples were carbonized at 350°C for 1 hour, 3 hours, and 8 hours in a nitrogen gas atmosphere under vacuum in a metal fixture. After cooling all three samples were ground in a coffee grinder for 30 seconds. After grinding the samples were evaluated for weight retention and tint strength. Each sample was mixed into a simple NR formulation and tested for ASTM D 5289 MDR Rheology and ASTM D 412 Unaged Physical Properties and compared with a Control compound using N550 furnace carbon black. The Control N550 batch and the best of the carbonized soy hull (CSH) samples were tested for ASTM D 2663 Phillips Dispersion Rating. The formulation used consists of 100 PHR SMR CV60, 18 PHR filler, 1PHR stearic acid, 5PHR zinc oxide, 1PHR TMQ, 1PHR sulfur, and 1PHR TBBS.

## Experiment I: Discussion and Results

Pictures of the 100% soybean hull pellets and the metal fixture can be found in Figures I and II.

**Figure I: Soybean Hull Pellets**

**Figure II: Metal Fixture**

The CSH samples can be found in Figures III through V.

**Figure III: 1 Hour**


**Figure 1V: 3 Hour**


**Figure V: 8 Hours**


The CSH weights can be found in Table I. The 8-hour sample had a very strong, pungent odor that smelled like char.

**Table I: Weights after Carbonizing**

| | Initial Weight, g | After Oven weight, g | % Weight Retention |
|---|---|---|---|
| 1 hour | 50 | 38.71 | 77.42% |
| 3 hour | 50 | 18.85 | 37.70% |
| 8 hour | 50 | 21.09 | 42.18% |

All the carbonized samples were ground in a coffee grinder for 30 seconds and pictures of the ground samples can be seen in Figures VI through VIII. Unlike carbon black, the CSH is not light, fluffy, and airborne which means it might not require pelletization. The CSH seemed to have an oily feel to it.

**Figure VI: 1 Hour**

**Figure VII: 3 Hour**

**Figure VIII: 8 Hour**

Examples of different types of pelletized carbon black can be found in Figures VI through XII.

**Figure IX: N990**

**Figure X: N650**

**Figure XI: N339**

A draw down test was done on the carbonized ground samples and the results can be found in Figures XII through XIV. This is a quick test to evaluate tinting strength and is done by smearing the black on a white piece of paper with one stroke. The 3- and 8-hour samples leave a darker smear than the 1-hour sample leading us to believe that the 1-hour sample is not actually carbonized.

Figure XII: 1 Hour

Figure XIII: 3 Hour

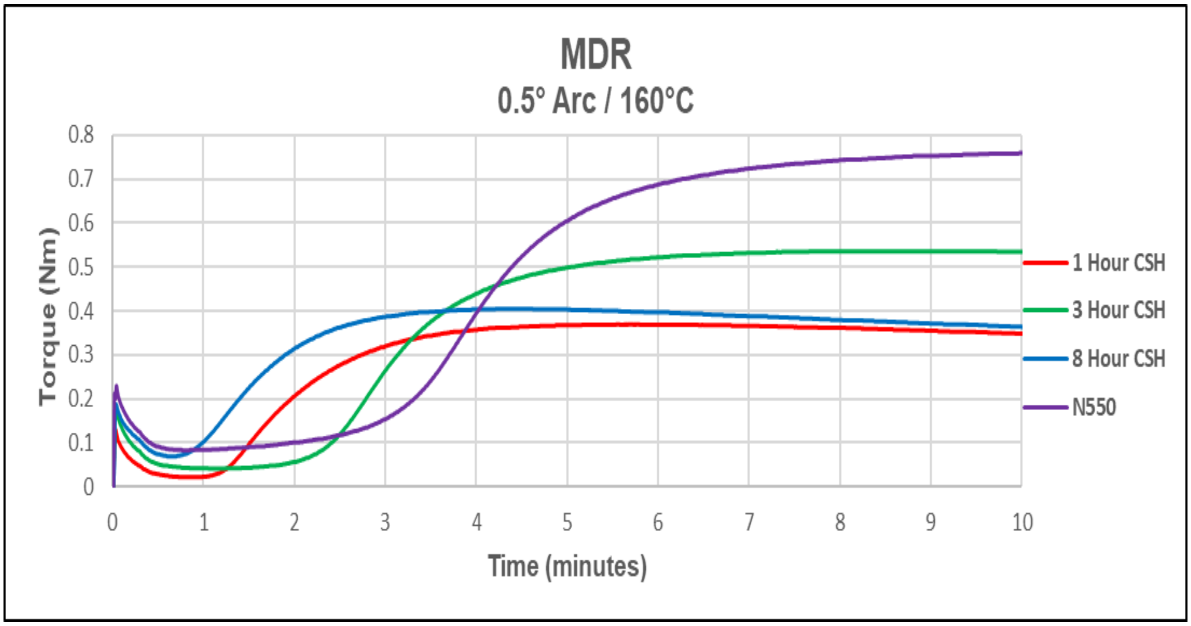
Figure XIV: 8 Hour

Each sample was mixed on a lab mill into a simple NR formulation outlined under Experiment I and compared to a Control compound using N550 furnace carbon black. ASTM D 5289 MDR rheology was tested at 176.6°C and the data can be found in Table II and the curve in Figure XV.

**Table II: Rheology Data**

| | Min Torque, ML, Nm | Cure Time, T50, min | Cure Time, T90, min | Scorch Time, TS1, min | Max Torque, MH, Nm |
|---|---|---|---|---|---|
| **1 Hour CSH** | 0.02 | 1.93 | 3.25 | 1.59 | 0.37 |
| **3 Hour CSH** | 0.04 | 3.07 | 4.68 | 2.57 | 0.54 |
| **8 Hour CSH** | 0.07 | 1.54 | 2.61 | 1.27 | 0.40 |
| **N550** | 0.08 | 4.07 | 6.12 | 3.20 | 0.76 |

**Figure XV: Rheology Curve**




The CSH had lower minimum torque, faster Ts1 time and T90 time, and lower maximum torque values. The lower maximum and minimum torque values may indicate the CSH is less reinforcing than the N550.

Each batch was cured into tensile slabs and tested for ASTM D 412 unaged physical properties and the data can be found in Table III.

**Table III: Unaged Physical Properties**

| | Control N550 | 1 Hour CSH | 3 Hour CSH | 8 Hour CSH |
|---|---|---|---|---|
| Tensile, MPa | 23.2 | 3.5 | 9.9 | 10.6 |
| 50% Modulus, MPa | 0.8 | 0.3 | 0.6 | 0.5 |
| 100% Modulus, MPa | 1.5 | 0.4 | 0.8 | 0.7 |
| 200% Modulus, MPa | 3.6 | 0.6 | 1.1 | 1.0 |
| 300% Modulus, MPa | 7.3 | 0.7 | 1.5 | 1.4 |
| Elongation, % | 582 | 692 | 681 | 721 |
| Durometer Shore A, points | 50 | 30 | 40 | 35 |

The N550 had the highest tensile properties. However, an improvement in tensile properties can be seen the longer the soy hull was carbonized. However, the 8-hour sample had lower modulus and durometer than the 3-hour sample. The 3-hour carbonized sample performed the best. It was closest to the N550 control in rheology, modulus, durometer, and elongation properties.

ASTM D 2663 Phillips Dispersion was run on the N550 Control and the 3-Hour Sample to determine if poor dispersion is why the CSH has inferior properties to the N550 or is it just less reinforcing. The Phillips dispersion data can be found in Table IV and pictures of the dispersion can be found in Figures XVI and XVII.

**Table IV: Phillips Dispersion**

| | N550 | 3 Hour CSH |
|---|---|---|
| Phillips Dispersion Rating | 7 | 1 |

**Figure XVI: N550 Dispersion**

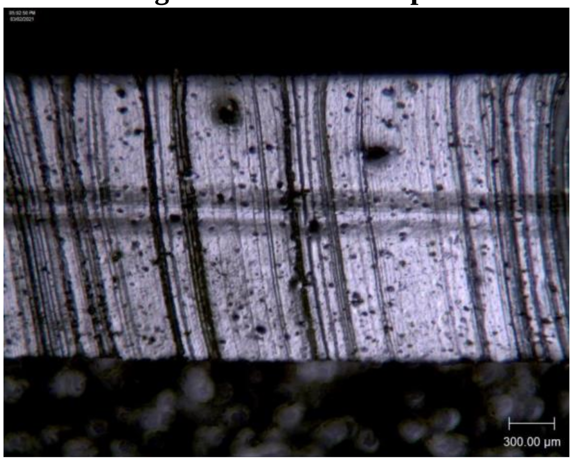
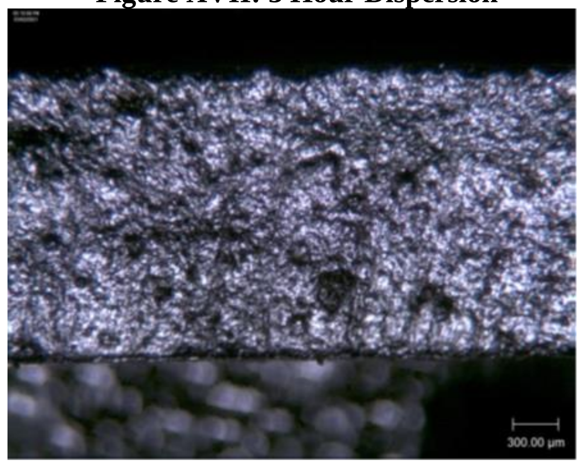



**Figure XVII: 3 Hour Dispersion**




The higher the dispersion rating the better the dispersion. The N550 Control had much better dispersion properties than the 3-hour carbonized sample. Phillips dispersion results indicate that the carbonized soybean hull had poor dispersion which is why it had inferior properties to the N550. A second experiment was run to see if extra grinding and washing of the CSH would improve the physical properties.

## Experiment II

In Experiment II the soy hull was ground before and after carbonizing, washed in toluene to remove any residual oil, and then dried. The soy hull was carbonized the same as the 3-hour sample from Experiment I. After the final grind the CSH was washed in toluene for 1 hour, strained, and then dried. The CSH was tested for ASTM D 6556 Nitrogen Adsorption, ASTM D 2414 DBP Absorption, ASTM D 1512 Carbon Black pH, and ASTM D 3849 Carbon Black Typing. Then the CSH was mixed into the same NR formulation from Experiment I and compared to N990, N762, N550, powdered N550, and a 75/25 blend of N550 and CSH and tested for ASTM D 5289 MDR rheology, ASTM D 412 Unaged Physical Properties, and ASTM D 792 Specific Gravity.

## Experiment II: Discussion and Results

Pictures of the ground soybean hull before and after carbonizing can be seen in Figures XVIII and XIX.

**Figure XVIII: Ground Soybean Hull**

**Figure XIX: Ground CSH**

The CSH was rinsed in toluene for 1 hour than strained and left to dry for 72 hours. Pictures of CSH in the toluene bath, the straining process, and dried can be found in Figures XX through XXIII.

Figure XX: Toluene Bath Figure XXI: Initial Strain Figure XXII Final Strain Figure XXIII: Dried




The amount of CSH retained after this process can be found in Table V.

**Table V: Retained CSH**

| | Weight Before, g | Weight After, g | % Retention |
|---|---|---|---|
| 3 Hour CSH | 200 | 83.89 | 41.95% |

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

**Table VI: DBP Absorption**

| SAMPLE ID | DBP ABSORPTION NUMBER $cm^3/100g$ |
|---|---|
| Carbonized Soybean Hull | 23.3 |

DBP Absorption is a test used to characterize the structure of a carbon black and this value is extremely low. It is even lower than N990 thermal black.

The CSH was tested for ASTM D 1512 Carbon Black pH and the data can be found in Table VII.

**Table VII: Carbon Black pH**

| SAMPLE ID | pH |
|---|---|
| Carbonized Soybean Hull | 9.04 |

pH of carbon black is tested to ascertain its effect on cure properties. The CSH has a similar pH as carbon black.

The CSH was tested for ASTM D 3849 Carbon Black Typing and the data can be found in Table VIII.

**Table VIII: Carbon Black Typing**

| Sample | Average Particle Size, nm | Standard Deviation, nm | n (Number of Particles Counted) | Maximum Particle Size, nm | Minimum Particle Size, nm | Estimated Type | ASTM Std. nm |
|---|---|---|---|---|---|---|---|
| Carbonized Soy Hulls | NA* | | 200 | | | NA* | |

The carbon black typing determined that the CSH does not show the characteristic grape cluster morphology that defines carbon black. Therefore, particle size was not determined. The samples were blocky and relatively featureless. Examples of normal carbon black morphology and the CSH morphology can be found in Figures XXIV and XXV.

**Figure XXIV: Carbon Black Morphology**

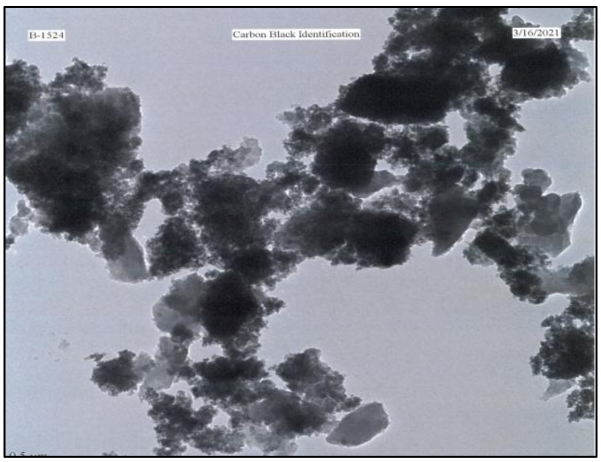
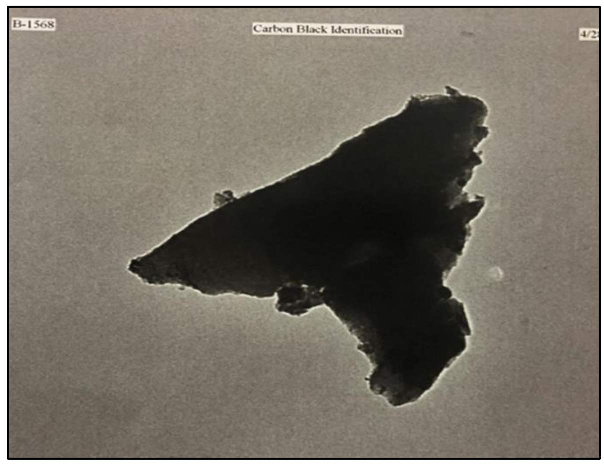



**Figure XXV: CSH Morphology**



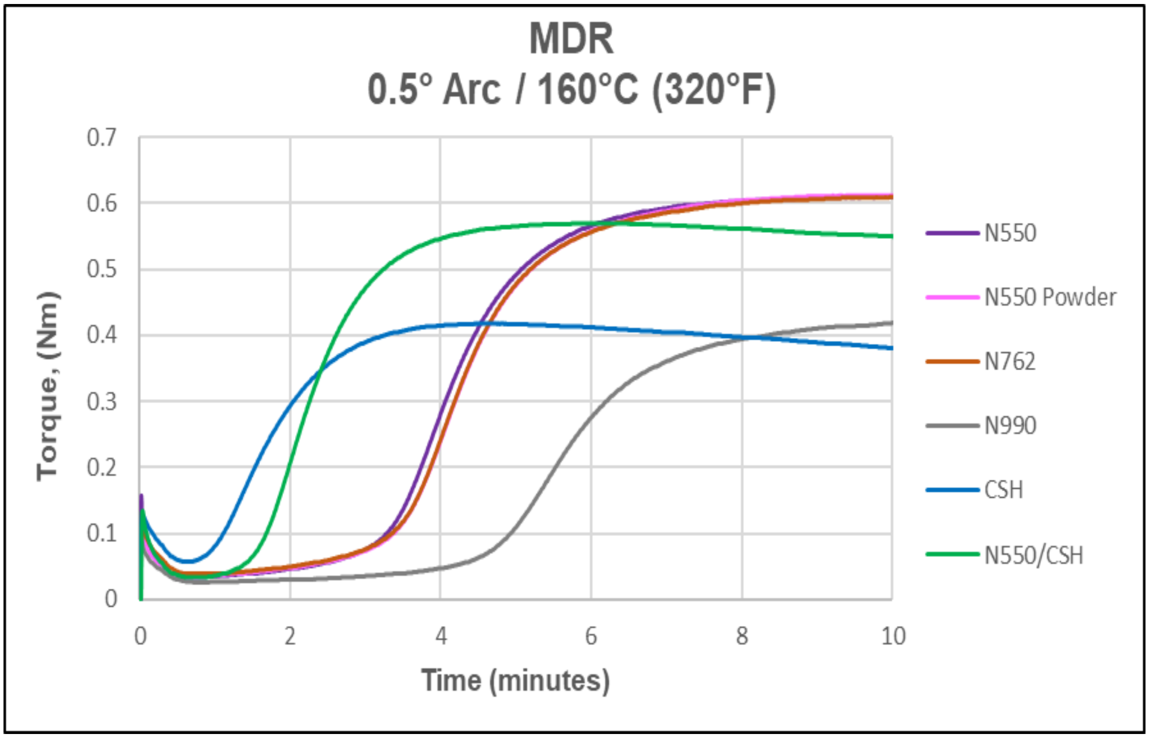

The CSH was also tested for ASTM D 6556 Nitrogen Adsorption and no value could be obtained.

The CSH and different carbon black controls N990, N762, N550, N550 powder (unpelletized), and a 75/25 blend of N550/CSH were mill mixed into the same natural rubber compound reported in Experiment I and tested for ASTM D 5289 MDR Rheology. The rheology data can be found in Table XI and Figure XXVI.

**Table IX: MDR Rheology (160°C, 0.5 ARC)**

| | Min Torque, ML, Nm | Cure Time, T50, min | Cure Time, T90, min | Scorch Time, TS1, min | Max Torque, MH, Nm |
|---|---|---|---|---|---|
| N550 | 0.03 | 4.12 | 5.68 | 3.52 | 0.61 |
| N550 Powder | 0.03 | 4.24 | 5.89 | 3.64 | 0.61 |
| N762 | 0.04 | 4.24 | 5.89 | 3.66 | 0.61 |
| N990 | 0.03 | 5.65 | 7.64 | 5.17 | 0.43 |
| CSH | 0.15 | 1.82 | 2.58 | 1.41 | 1.36 |
| CSH / 550 Blend | 0.03 | 2.25 | 3.40 | 1.83 | 0.57 |

**Figure XXVI: Rheology Curve**



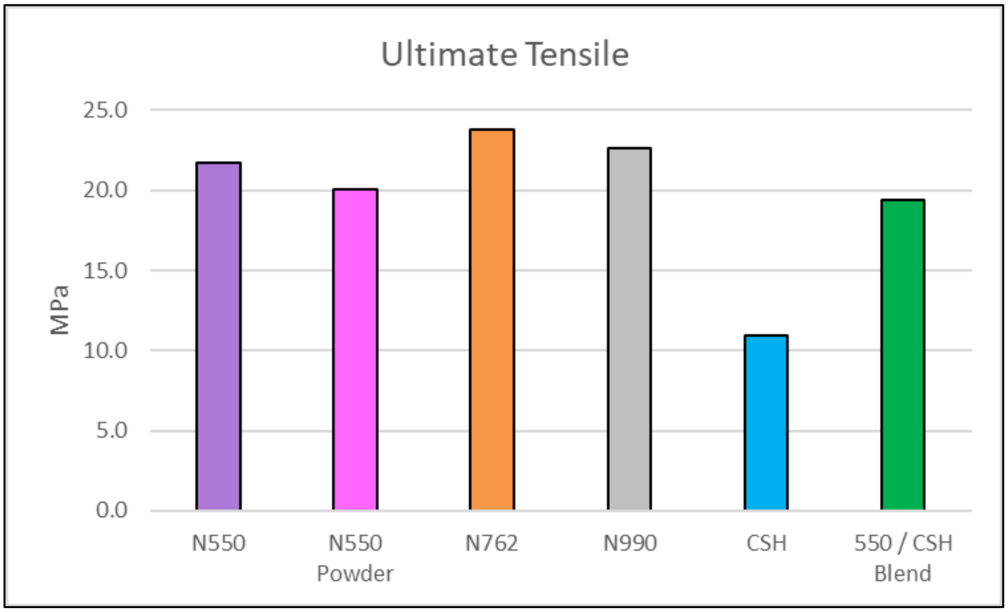

The N990, N762, and N550 are standard grades of pelletized carbon black. The powder N550 is carbon black that was not pelletized. CSH is 100% carbonized soy hull and the N550/ CSH is a 75/25 blend. The N762, N550, and Powder N550 had similar maximum torque properties. The blend had slightly lower properties than the N550. The 100% CSH had similar maximum torque properties as the N990. The N990 had the slowest T90 and Ts1 times because it is a thermal black made from natural gas and has no residual sulfur in it. The 100% CSH had the fastest T90 and Ts1 times.

Each batch was tested for ASTM D 412 unaged physical properties and the data can be found in Table X and Figures XXVII through XXX.

**Table X: Unaged Physical Properties**

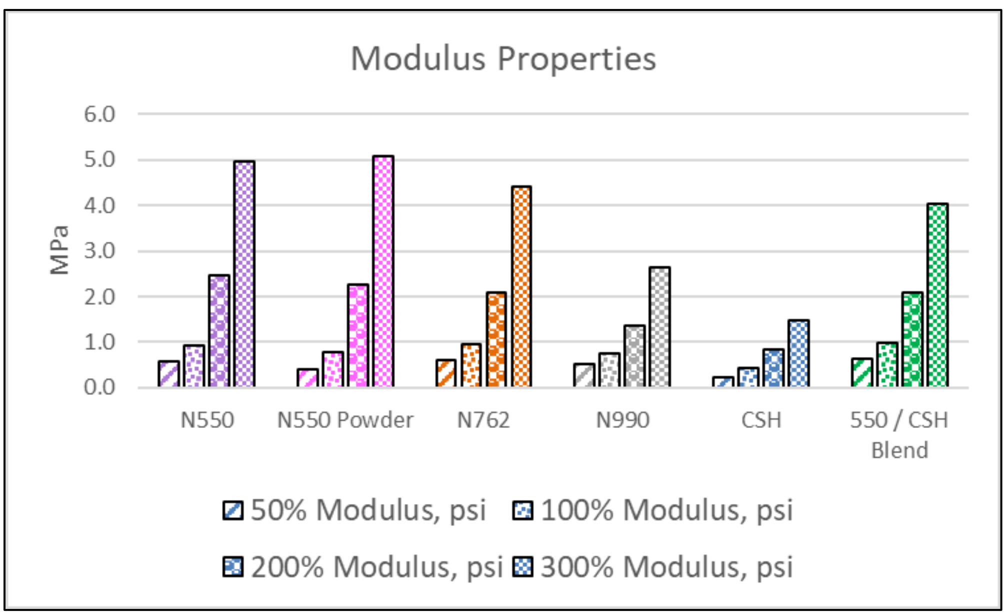
| | N550 | N550 Powder | N762 | N990 | CSH | 550 / CSH Blend |
|---|---|---|---|---|---|---|
| Tensile, psi | 21.7 | 20.0 | 23.8 | 22.7 | 10.9 | 19.4 |
| 50% Modulus, psi | 0.6 | 0.4 | 0.6 | 0.5 | 0.2 | 0.6 |
| 100% Modulus, psi | 0.9 | 0.8 | 0.9 | 0.8 | 0.4 | 1.0 |
| 200% Modulus, psi | 2.5 | 2.2 | 2.1 | 1.4 | 0.8 | 2.1 |
| 300% Modulus, psi | 5.0 | 5.1 | 4.4 | 2.6 | 1.5 | 4.0 |
| Elongation, % | 612 | 573 | 650 | 686 | 682 | 607 |
| Durometer Shore A, points | 41 | 45 | 40 | 35 | 40 | 41 |

**Figure XXVII: Tensile Properties**



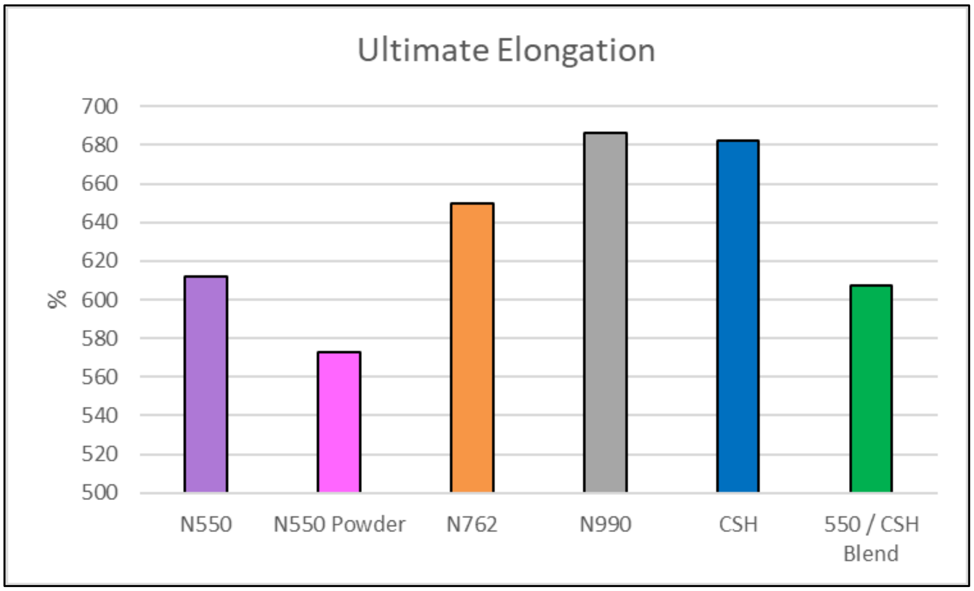

The CSH compound has the lowest tensile properties. Surprisingly, the N762 had the highest tensile properties. The powdered N550 had lower tensile properties than the pelletized N550 which you would expect because it is harder to disperse into a rubber compound. The blend had lower tensile properties than the pelletized N550 and slightly lower tensile properties than the powdered N550. The blend had much better tensile properties than the 100% CSH compound.

**Figure XXVIII: Modulus Properties**



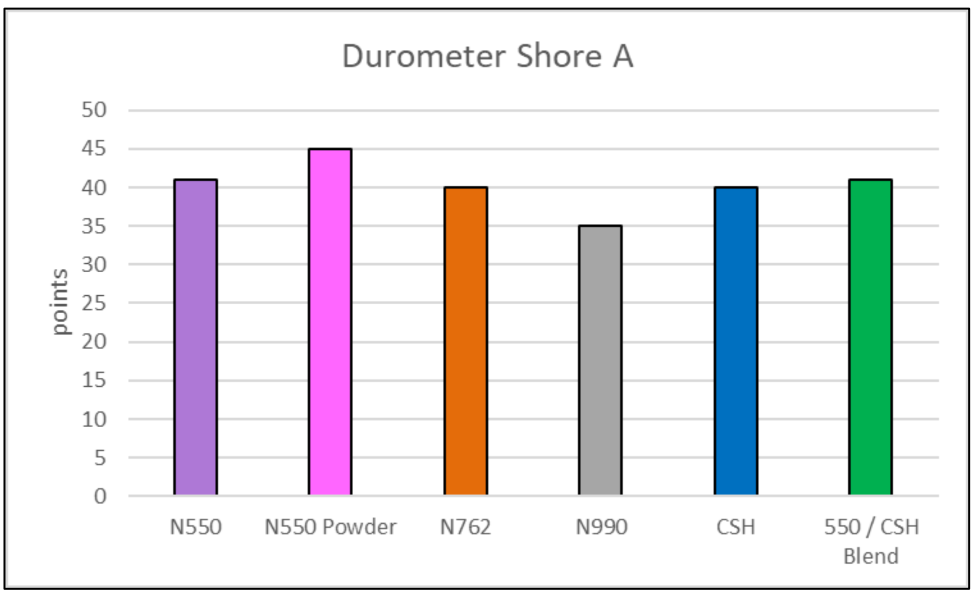
The CSH had the lowest modulus properties and the N550 had the highest modulus properties which is what you would expect. The Blend had similar 50% and 100% modulus as both N550 carbon blacks.

**Figure XXIX: Elongation Properties**




The N990 and the CSH have the highest elongation properties. The blend has similar elongation as the pelletized N550. The powdered N550 has lower elongation properties indicating it may have poorer dispersion.

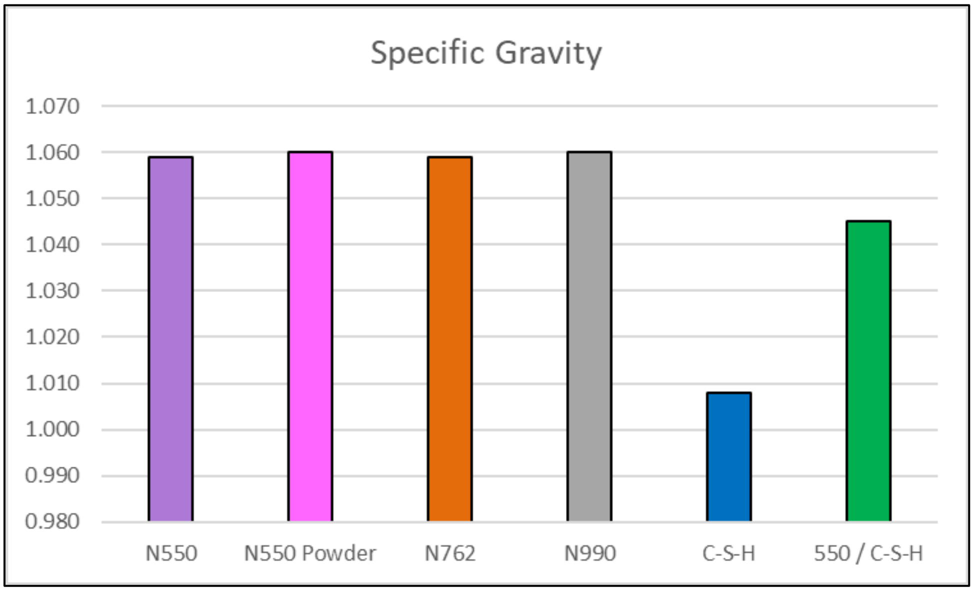
**Figure XXX: Durometer Properties**




The N990 has the lowest durometer properties and the powdered N550 has the highest. The blend has similar durometer properties as the pelletized N550. In Experiment I the CSH had much lower durometer than the N550 which means using the toluene bath to remove any excess oil worked.

Each batch was tested for ASTM D 792 specific gravity and the data can be found in Figure XXXI.

**Table XXXI: Specific Gravity**




The CSH has a lower specific gravity than carbon black which would allow for weight reduction in the end rubber product.

## Conclusion

Soybean hull can be successfully carbonized and used as a partial replacement for carbon black. The added grinding and toluene wash in experiment II improved the 100% CSH durometer. A partial blend of CSH and N550 saw little to no reduction in physical properties. Carbonized soybean hull has a lower specific gravity which could offer weight reduction opportunities in the end product. Carbonized soybean hull is a partial carbon black replacement that is not indexed to the price of oil, is not regulated by the EPA, is not a carcinogen, is sustainable, and will not affect the food supply.

*Disclaimer: This paper has not been peer reviewed.*

## Acknowledgements

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