

Improved Carbon Blacks for Low Hysteresis Applications in Rubber

Leszek Nikiel*, Wesley Wampler, Henry Yang, and Tom Carlson
Sid Richardson Carbon & Energy Company
4825 North Freeway, Fort Worth, TX

Presented at the Fall 172nd Technical Meeting of the
Rubber Division of the American Chemical Society, Inc.
Cleveland, OH
October 16-18, 2007

ISSN: 1547-1977

*speaker

Abstract

Tires and other rubber goods are employed in many applications that require dynamic deformations and thus the relative amount of energy that is stored or lost as heat during the deformations is important in assessing the performance of the rubber good. While the polymer and different chemicals play a significant role in this, the carbon black is a very important contributor to this balance. Carbon blacks that can impart less energy loss in the form of heat at the same level of reinforcement as a similar carbon black are known as low hysteresis carbon blacks. Carbon blacks have been developed and will be discussed in this paper that exhibit this low hysteresis behavior and represent advanced fillers.

Introduction

Increasing energy prices are forcing both consumers and manufacturers to look for better technologies in order to conserve energy, keep the cost under control, and preserve as much as possible of the non renewable natural resources. The above statement applies also to tire manufacturers. Development of new, less hysteretic materials for tire application is one of the important focus areas of each tire manufacturer. Tires are an important part of the energy conservation process. As far as tires are concerned, the experiments and theoretical calculations are showing that as much as 70% of the rolling resistance originates from the tread region of the tire and the remaining 30% from other tire components¹. Since filled rubber compound typically contains a significant amount of filler, its influence on compound hysteresis is important. However, when developing new fillers such as carbon black for tire applications it is good to be mindful of the many performance parameters affected by the filler as well as many basic functions of the pneumatic tire². The tire must provide load carrying capacity, transmit driving and braking torque, provide steering response, produce cornering forces and minimize road noise and vibrations. In addition, it must resist abrasion, have low rolling resistance and, of course, be durable and safe. Furthermore, the tire has many components which contain different types of compounded rubber to optimize the properties for that part of the tire. Typical components include the tread, sidewall, shoulder, bead, plies, belts, liner and chafer. For the new carbon blacks described herein, we have chosen to simply classify them as tread and non-tread, which will become clearer as the paper develops. In designing a new carbon black for any of these components one has to understand not only its function but also where improvements can be made.

The tread section of the tire is where contact between the road and the vehicle is made. The rubber in this area must be compounded so it provides the right balance of wear resistance, heat buildup (hysteresis) and traction. The tread is normally a blend of different synthetic rubbers and/or natural rubber that also contains carbon black, oil, curatives, antioxidants and other chemicals. Depending on the application, the balance of wear resistance, hysteresis and traction is modified through the different raw materials with carbon black being one of the most critical. The new tread carbon black presented

in this paper is for applications in which hysteresis and traction are given more priority in the balance.

In the non-tread sections of the tire there is concern about many other performance properties of the rubber compound that affect the tires durability, ride comfort, handling, etc. The sidewall is the portion of the tire between the beads and the tread that control the ride and offer support. It is usually compounded to give high flexibility and weather resistance. The shoulder is the upper portion of the sidewall just below the edge of the tread. It is critical for such tire properties as cornering and heat development thus the rubber in this section is compounded to optimize these characteristics. The bead is a structure composed of high tensile strength; bronze plated steel wire that is wound to form a continuous strand, which is then coated with rubber and functions as an anchor for the plies and holding the tire on the rim of the wheel. Each steel wire is encapsulated by a special rubber compound that helps in uniformly distributing stresses among the wires and combines them into a strong flexible component. The carcass plies are rubber coated layers of fabric cord that extend from bead to bead reinforcing the tire. The rubber compound for the plies is spread onto the fabric in an operation known as calendaring and the rubber compound is designed to provide little or no shrinkage, tackiness appropriate for the adhesion to the fabric, and proper viscosity so that it is applied uniformly to the fabric. The belts are directly under the tread and consist of tire cord (fabric or steel) imbedded into a rubber compound whose function is to restrict or hold the carcass plies and to help resist deformation in the tire footprint. The liner is the innermost layer of rubber and is a thin layer that prevents the compressed air from escaping. This is obviously a special compound that must have low air permeability but also other properties such as good thermal/oxidative stability and good adhesion to the body stock. The chafer is a narrow strip of yet another rubber compound that protects the cord from the rim and helps distribute flex above the rim.

The point of reiterating all these well known components of a tire is to illustrate that they require many special compounds and that each plays a role in the performance of the tire. The new non-tread black being introduced brings a special blend of carbon black properties not available through known grades or blends of grades and might provide additional enhancements in performance not previously realized. It provides a unique combination of high modulus/hardness, low heat buildup (hysteresis), ease of mixing and good processability. Many of the compound performance properties are expected due to known relationships between carbon black properties and compound properties³ but this non-tread black provides a combination of properties not found before in a commercial carbon black or possible in a blend of carbon blacks leading to its unique properties.

Experimental

Today, most of the carbon black used in the tire industry is produced using the furnace process. In this process, the feedstock oil is combusted in non-stoichiometric reaction to form a very finely divided material composed of aggregates that are the carbon black monounits. These aggregates are typically submicron in size and of very complex shape. The surface of aggregates is covered with turbostratic graphite crystallites and areas of disorganized and amorphous carbon. When carbon black is

formed in the reactor, it is in the form of powder with apparent density of about 10^{-2} g/cm³. In order to be shipped and further processed, it is necessary to densify it. This process is usually achieved through a pelletization. The finished pellets are quasispherical with a diameter in the millimeter range and an apparent density of about 0.35 g/cm³. In order to produce different grades of carbon black, different reactor technology is employed. As a general rule, tread grade blacks are produced using different reactor design as compared to carcass grades. In addition to specific reactor design, the number and position of oil spraying nozzles, the ratio of air to oil and natural gas, as well as the quenching water position also plays a critical role. In most cases, carbon black properties are set in the reactor during a few millisecond reaction time, the rest of the production time, which could add additional two hours to the production process, is just a mechanical handling of the product.

The new carbon blacks presented in this study, SR401 (non-tread) and SR129 (tread) were produced using special reactor technology and are commercially available from Sid Richardson Carbon Co. (SRCC). The ASTM grades they are being compared to were also produced by SRCC. They have been tested for analytical properties using ASTM test methods and this data is presented in Table 1 and Table 2 alongside control carbon blacks for the studies in rubber. Aggregate size distribution measurements were made on a disk centrifuge sedimentometer (Brookhaven BI-DCP). Rubber mixing was done on either 6" roll mills or a Reliable R-40 internal mixer using ASTM formulation D3191 (SBR recipe, 50 phr black), ASTM D3192 (NR recipe, 50 phr black), SRCC Passenger Tread Formula (SBR/BR recipe 65 phr black). These recipes are given in Table 3. For the SR401 studies the D3192 recipe was also studied at various loadings of carbon black. Rubber testing was done by ASTM methods except for low strain dynamic properties (performed on the Rheometrics ARES system), angle abrasion index (performed on the SRCC angle abrasion tester), acoustic spectroscopy to measure high frequency behavior to predict traction using SRCC developed equipment⁴⁻⁵ operating at 1 MHz frequency.

Results and Discussion

The SR129 carbon black is the first from the series of low hysteresis carbon black presented in this paper. Based on ASTM D1765, the SR129 is classified as a 100 series black. There is no direct ASTM equivalent to SR129. As is indicated in Fig. 1 the ASTM black with closest analytical properties is N121. In addition to N121, N234, N299, and N110 were used to compare the rubber properties in three different formulations mentioned above. The data are presented in Figs. 2-8. As expected from analytical properties the 100%, 200%, and 300% modulus is higher than any of the blacks used for comparison (see Fig. 2). One could expect that the tensile properties will be sacrificed. What is evident on Fig. 3 is quite opposite; tensile is higher when compared in model tread formula. Mooney viscosity is usually increasing with the increased structure of carbon black. In case of SR129, it is lower as compared to our control blacks in D3191, and model tread formulations and only slightly higher in D3192 formulation (see Fig. 4). This black disperses in rubber better than other blacks used in this study. Good dispersion, at least partially, could be attributed to high structure. What make this black a truly unusual product is its excellent hysteresis properties. Both rebound and $\tan \delta$ as well

as G''_{MAX} indicate 6-13 % better hysteresis as compared to control blacks (see Figs. 3-7). This level of hysteresis was obtained due to special reactor design leading to wider aggregate size distribution as compared to other ASTM grades (Fig. 9). In order to assess traction performance, the high frequency technique described previously was used. These data indicate better or equivalent properties as compared to control blacks. The only tire parameter that is sacrificed is tread wear. As expected for high structure and wide aggregate size distribution black, the abrasion properties are slightly worse as compared to our control blacks. In certain applications the significant gain in the hysteresis performance could offset the abrasion loss.

The SR401 carbon black is an N400 series carbon blacks based on the ASTM classification. There are very few carbon blacks in this area, which is considered intermediate between tread grades and carcass grades. There are no other carbon blacks in this surface area range with such unusually high structure. This carbon black has a high oil absorption number (OAN) of about 170 which it is well known leads to higher viscosity, higher modulus, higher hardness, less die swell and better processability in the compounds to which it is dispersed. Not only does it have unique analytical properties but it is made in a proprietary method that provides it with a wide aggregate size distribution that enables it to impart excellent hysteresis properties in the polymers to which it is added. Demonstration of this wide aggregate size distribution is shown in Figure 10. In order to demonstrate its properties in rubber a comparison was made versus a low surface area tread grade (N330) and a high surface area carcass grade (N550). The polymer chosen was natural rubber due to its widespread use in tires and the loading was varied from 40 to 60 phr to show how the SR401 could provide certain properties at lower loadings if required. The samples were then tested for rheometer, stress-strain, viscosity, hardness, rebound and low strain dynamic properties. This data is shown graphically in Figures 11-18.

Several comments from the data for SR401 are worth noting. The green strength, as measured by ML at 160 C shows the SR401 to be in between N330 and N550 at low loadings but at higher loadings it has the highest green strength (Figure 11). The stiffness of the compound as measured by the rheometer MH is higher at all loadings and it is noted that about 10 phr less SR401 gives similar stiffness with N550 and about 5 phr less compared to N330 (Figure 12). The time to 90% cure state is more stable at various loadings for the SR401. Mooney viscosity, durometer hardness, and 300% modulus are also higher at all loadings compared to the closest tread and carcass grade (Figs 13-15). These compound properties are due to SR401's high structure. Die swell, as measured by relative extrusion mass, is less at all loadings again related to the high structure (Figure 16). Though no actual measurements of processability were recorded, it was observed in the lab that the SR401 was an easy mixing compound which would provide its own benefits. Elongation was lower at most loadings however at the 40 phr it was almost equivalent to N550. As expected, the hysteresis as measured by % rebound and low strain dynamic properties was intermediate for SR401 compared to N330 and N550 (Figures 17 and 18). However based on its specific surface area it would be expected to be a little closer to N330 than observed leading to the notion that SR401 does provide an improved hysteresis in rubber compounds.

Conclusions

New low hysteresis carbon blacks have been developed for tire applications and are known as SR129 and SR401. SR129 is for tread applications and has been shown to be excellent for hysteresis and traction. The higher structure and wider aggregate size distribution of SR129 help produce these improvements. SR401 has high structure, wide aggregate size distribution and specific surface area intermediate between tread and traditional carcass grades. It has been developed for non-tread rubber applications where the unique properties of this grade can be utilized. Due to its high structure it imparts a relatively high modulus and hardness while giving relatively low hysteresis due to its wide aggregate size distribution and low specific surface area. Fast mixing, easy incorporation and good processing are expected advantages of the high structure SR401 in large mixing operations. Thus SR401 could be used almost anywhere in the non-tread section of the tire due to its good processing and low hysteresis.

Acknowledgements

The authors would like to thank Sid Richardson Carbon Co. for permission to publish this paper. Rubber mixing and testing were performed by Del Blue, Patrick Nichols and Mitch Sanders. Aggregate size distribution measurements were done by David Roberts. Analytical testing on the carbon black was performed by Ron Ellis and Steve Break.

This information is provided as a convenience and for informational purposes only. No guarantee or warranty as to this information, or any product to which it relates is given or implied. This information may contain inaccuracies, errors or omissions and Sid Richardson DISCLAIMS ALL WARRANTIES EXPRESS OR IMPLIED, INCLUDING MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE AS TO (i) SUCH INFORMATION, (ii) ANY PRODUCT OR (iii) INTELLECTUAL PROPERTY INFRINGEMENT. In no event is Sid Richardson responsible for, and Sid Richardson does not accept and hereby disclaims liability for, any damages whatsoever in connection with the use of or reliance on this information or any product to which it relates.

References

1. L. Nikiel, M. Gerspacher, H. Yang, and C. P. O'Farrell, '*Filler Dispersion, Network Density, and Tire Rolling Resistance*', Rubber Chem. and Technol. **74** (2001) 249.
2. F.J. Kovac in "*Science and Technology of Rubber*" edited by F.I. Eirich, Chapter 14 (*Tire Manufacturing and Engineering*), pages 569-607, Academic Press (1978).
3. W.A. Wampler, T.F. Carlson and W.R.Jones in "*Rubber Compounding – Chemistry and Applications*" edited by B. Rodgers, Chapter 6 (*Carbon Black*), pages 239-284, Marcel Dekker Inc.(2004).
4. M. Gerspacher, C. P. O'Farrell, L. Nikiel, F. Le Mehaute, and H. H. Yang, '*High Frequency Viscoelasticity of Carbon Black Filled Compounds*', Rubber Chem. and Technol. **69** (1996) 786.
5. M. Gerspacher, C. P. O'Farrell, L. Nikiel, and H. H. Yang, '*Properties of carbon black-filled compounds*', Rubber&Plastic News, August 26, (1996) 39-40.
6. L. Nikiel, H.H. Yang, T.F. Carlson and W.A. Wampler, '*Role of Fillers in Elastomeric Matrices. New Advanced Testing Methods*', Paper No. 13, Presented at the 167th Technical Meeting of the Rubber Division, American Chemical Society, San Antonio, TX, May 16-18, 2005.

Table 1

Analytical Properties of SR129 in comparison to other ASTM Grades

Grade	<u>SR129</u>	<u>N121</u>	<u>N234</u>
OAN, cc/100g	140	132	125
COAN, cc/100g	112	111	103
Iodine No., g/kg	117	121	120
N2SA, m2/g	112	122	119
Tint, % ITRB	108	119	123

Table 2

Analytical Properties of SR401 in comparison to other ASTM Grades

Grade	<u>SR401</u>	<u>N550</u>	<u>N330</u>
OAN, cc/100g	170	121	102
COAN, cc/100g	105	86	88
Iodine No., g/kg	58	43	82
N2SA, m2/g	62	41	79
Tint, % ITRB	77	56	104

Table 3

Rubber Formulations

D3191

<u>Ingredient</u>	<u>phr</u>
SBR 1500	100.00
Zinc Oxide	3.00
Sulfur	1.75
Stearic Acid	1.00
Carbon Black	50.00
TBBS	1.00

D3192

<u>Ingredient</u>	<u>phr</u>
Natural Rubber	100.00
Zinc Oxide	5.00
Sulfur	2.50
Stearic Acid	3.00
Carbon Black	50.00
Benzothiazyl disulfide	0.60

SRCC Passenger Tread

<u>Ingredient</u>	<u>phr</u>
SBR 1712	96.25
Budene 1254	37.50
Carbon Black	65.00
Zinc Oxide	3.00
Stearic Acid	2.00
6PPD	1.50
Aromatic Oil	3.75
Sulfur	1.80
CBS	1.20
DPG	0.10

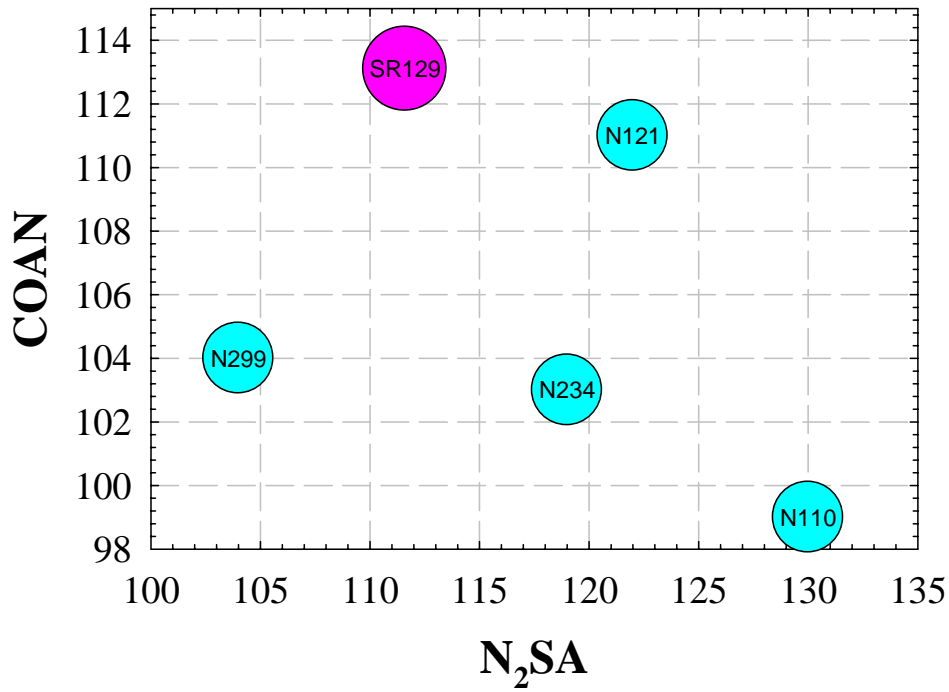


Figure 1. Analytical properties (COAN and N₂SA) of SR129 plotted against selected ASTM grades.

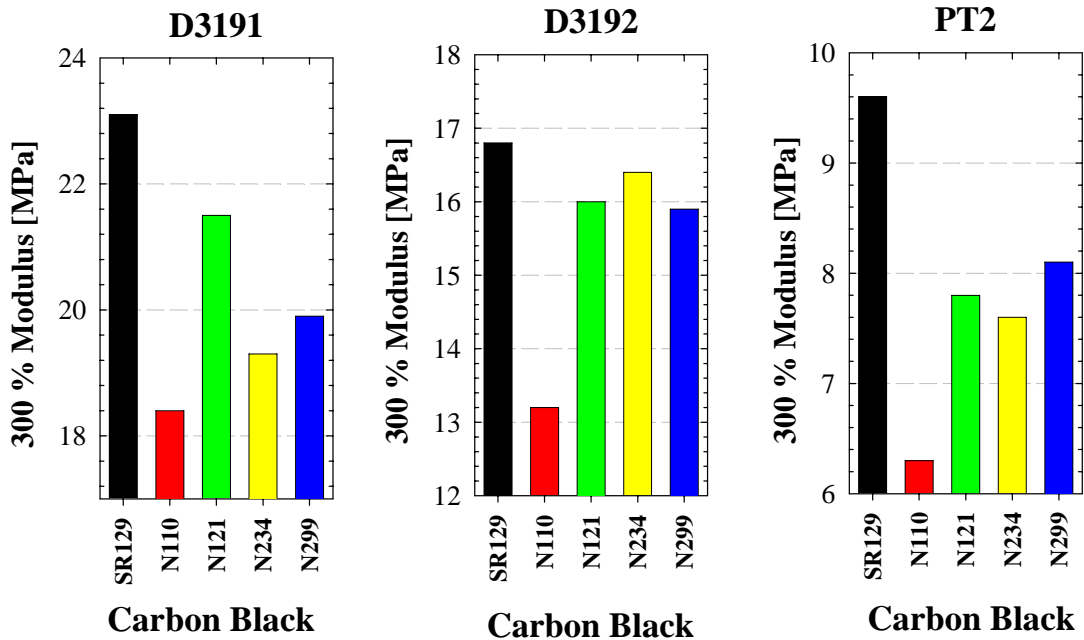


Figure 2. 300% Modulus obtained for SR129 vs. N110, N121, N234, and N299. ASTM D3191, ASTM D3192, and Model Tread Formulation PT2 were used.

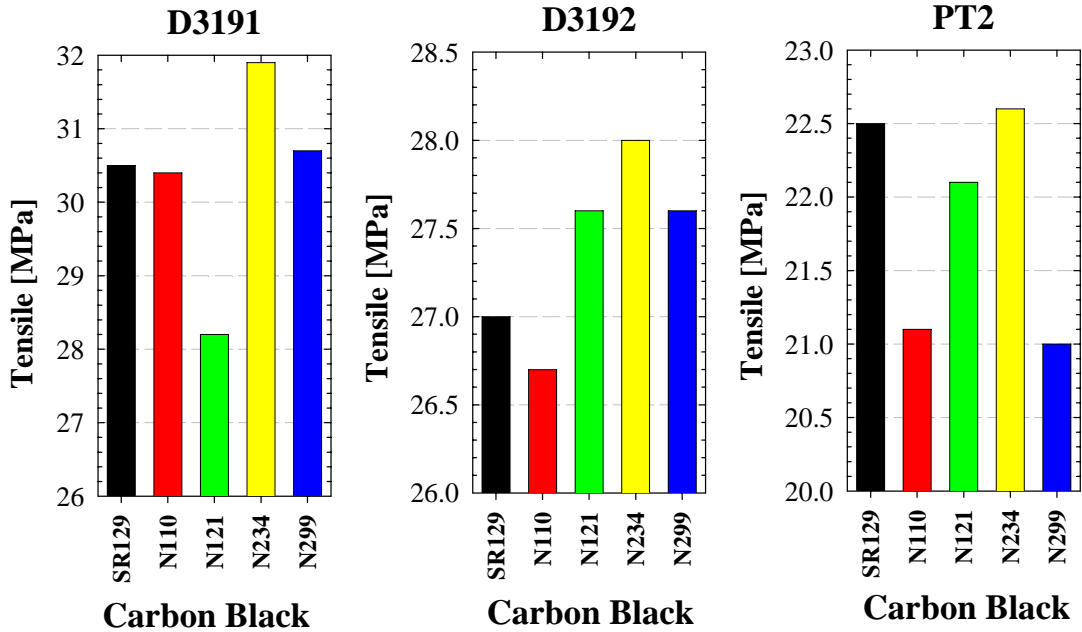


Figure 3. Tensile properties obtained for SR129 vs. N110, N121, N234, and N299. ASTM D3191, ASTM D3192, and Model Tread Formulation PT2 were used.

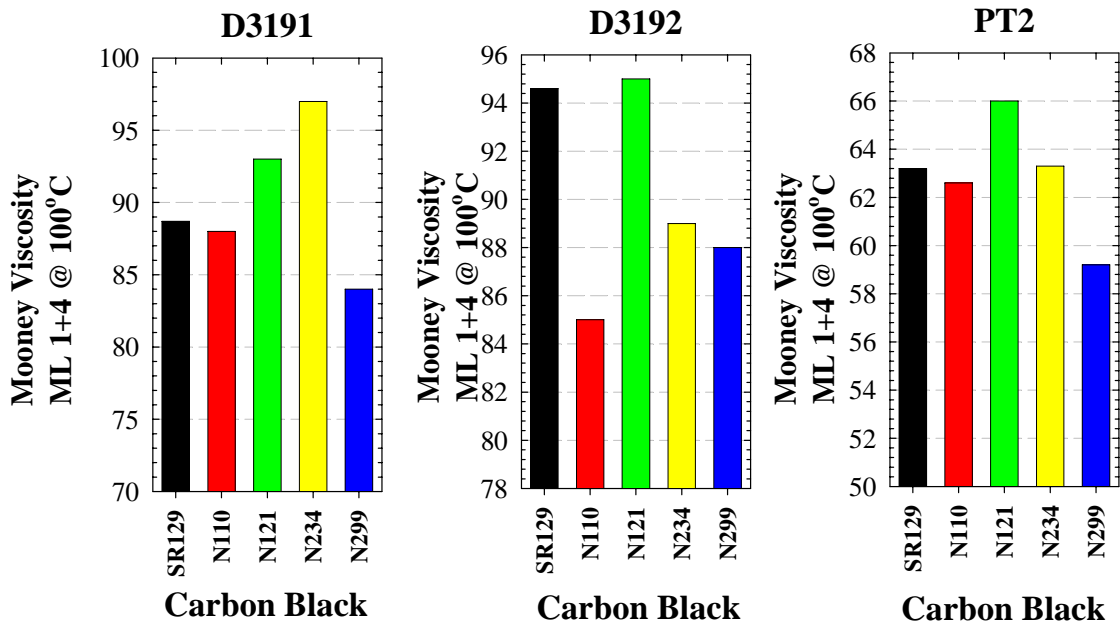


Figure 4. Mooney Viscosity obtained for SR129 vs. N110, N121, N234, and N299. ASTM D3191, ASTM D3192, and Model Tread Formulation PT2 were used.

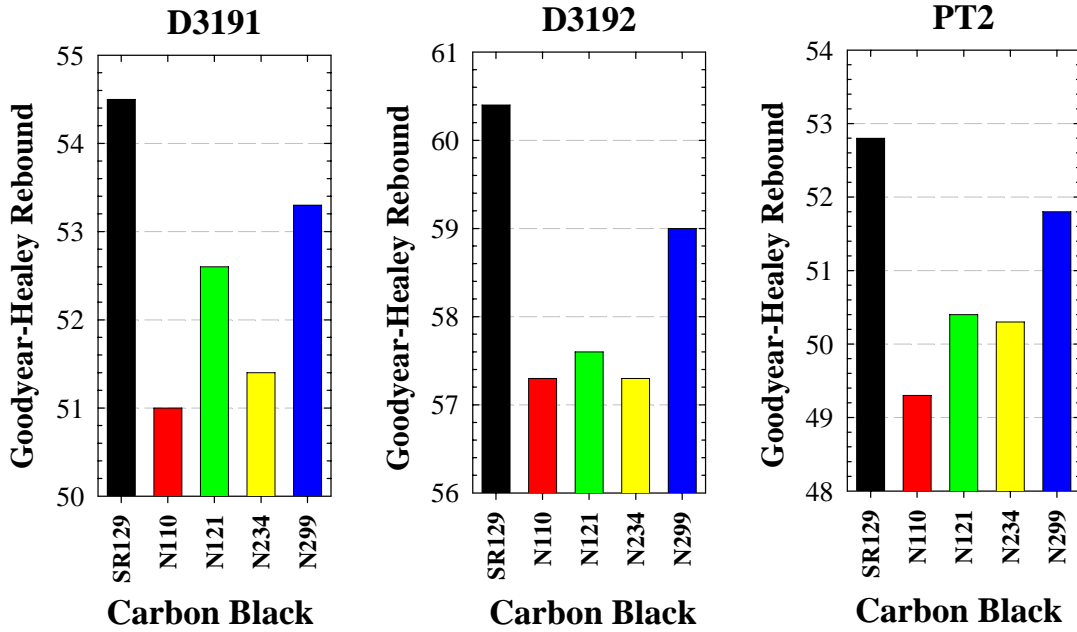


Figure 5. Rebound obtained for SR129 vs. N110, N121, N234, and N299. ASTM D3191, ASTM D3192, and Model Tread Formulation PT2 were used.

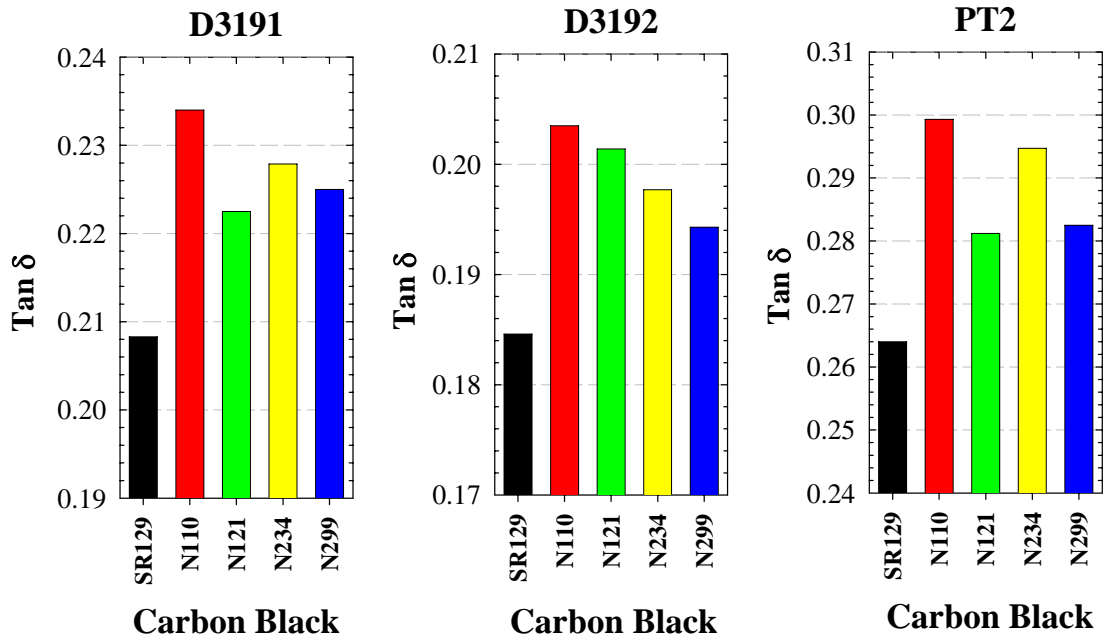


Figure 6. Tan delta obtained for SR129 vs. N110, N121, N234, and N299. ASTM D3191, ASTM D3192, and Model Tread Formulation PT2 were used.

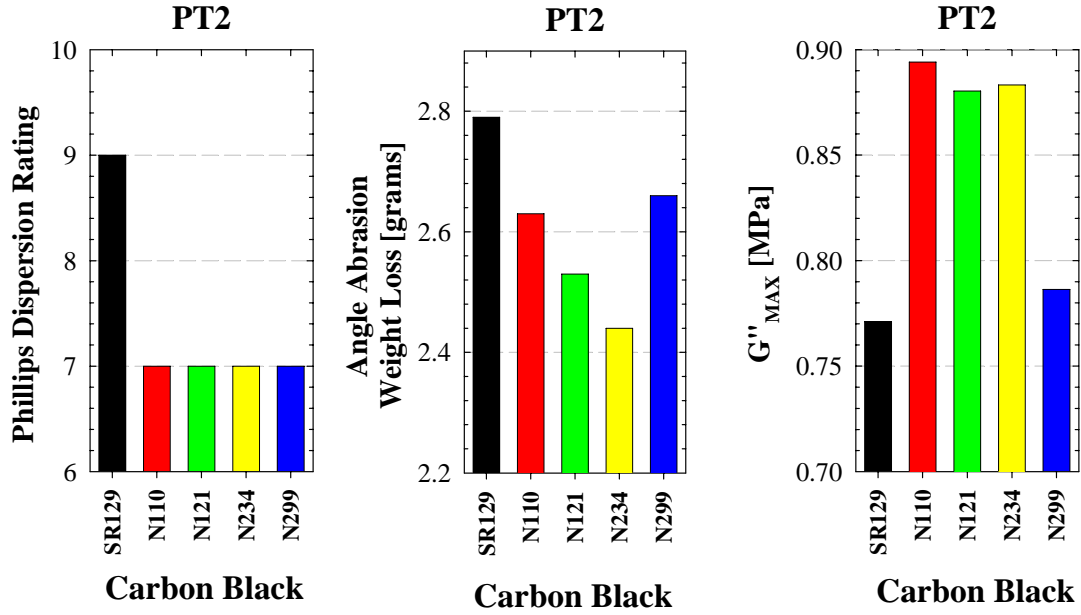


Figure 7. Phillips dispersion, angle abrasion weight loss, and G''_{MAX} obtained for SR129 vs. N110, N121, N234, and N299. Model Tread Formulation PT2 was used.

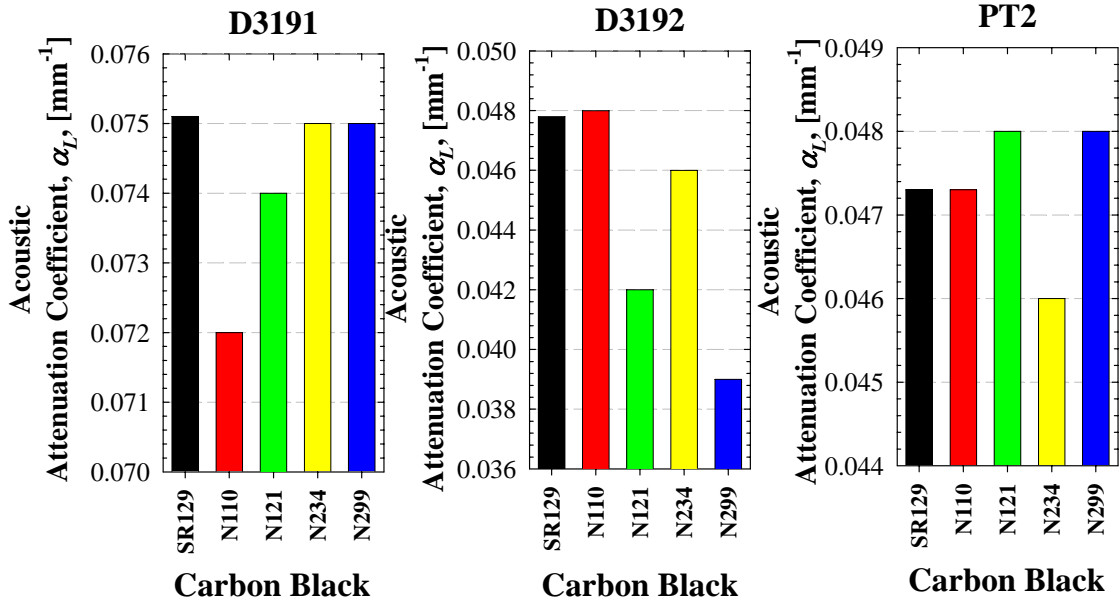


Figure 8. Attenuation Coefficient obtained for SR129 vs. N110, N121, N234, and N299. ASTM D3191, ASTM D3192, and Model Tread Formulation PT2 were used.

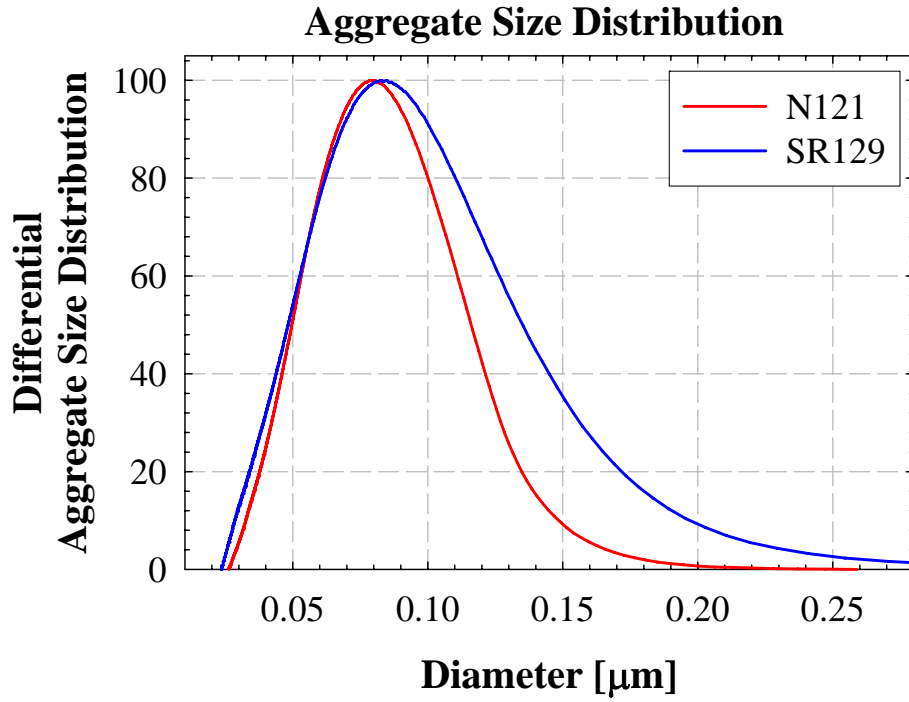


Figure 9. Aggregate size distribution data obtained for SR129 vs. N121.

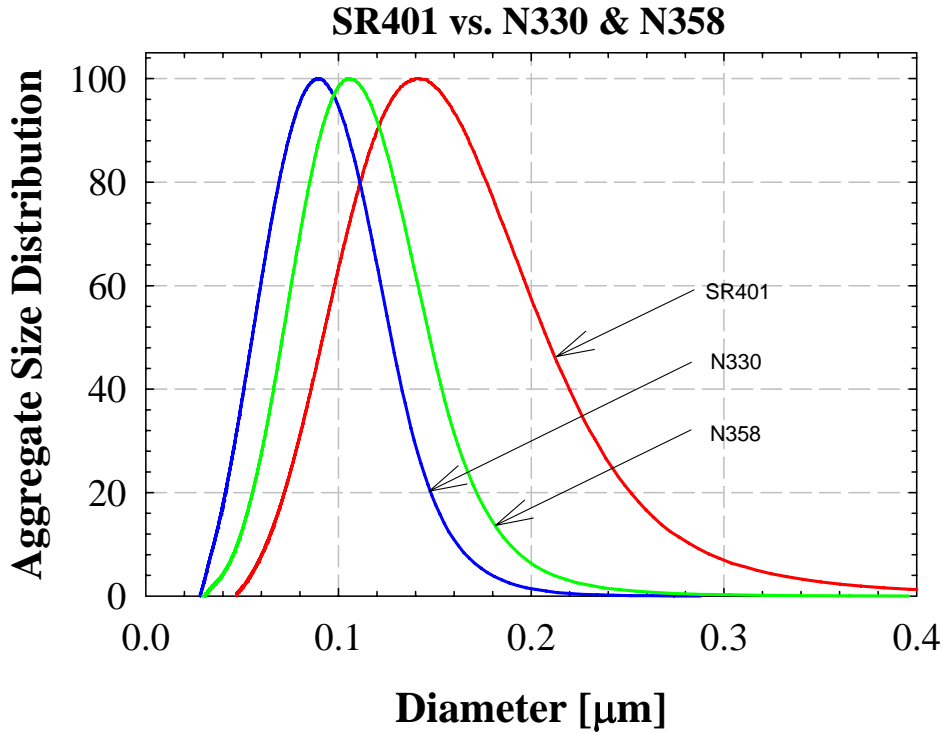


Figure 10. Aggregate Size Distribution Data for SR401 versus two N300 series grades with medium structure (N330) and high structure (N358)

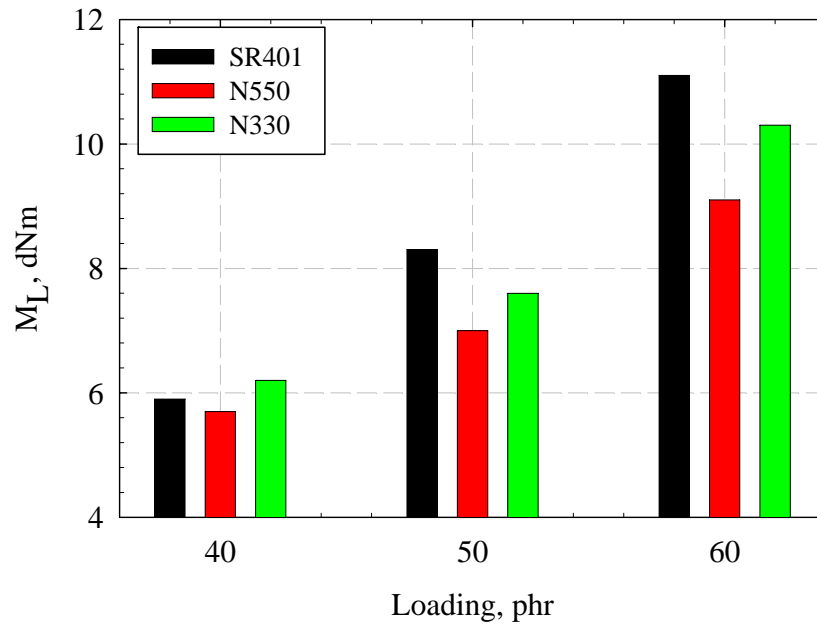


Figure 11. ML for SR401 vs N550 and N330. Loading Study in Natural Rubber (Modified D3192)

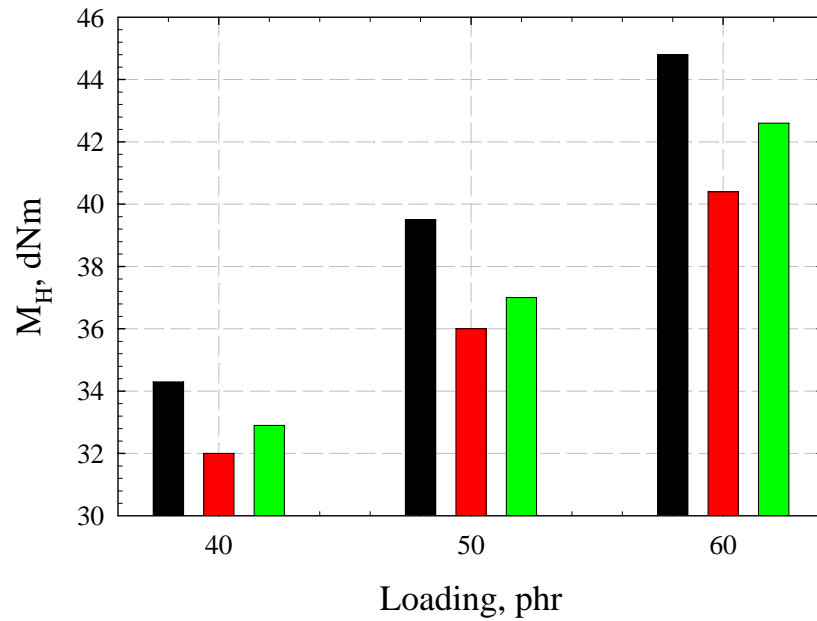


Figure 12. MH for SR401 vs N550 and N330. Loading Study in Natural Rubber (Modified D3192)

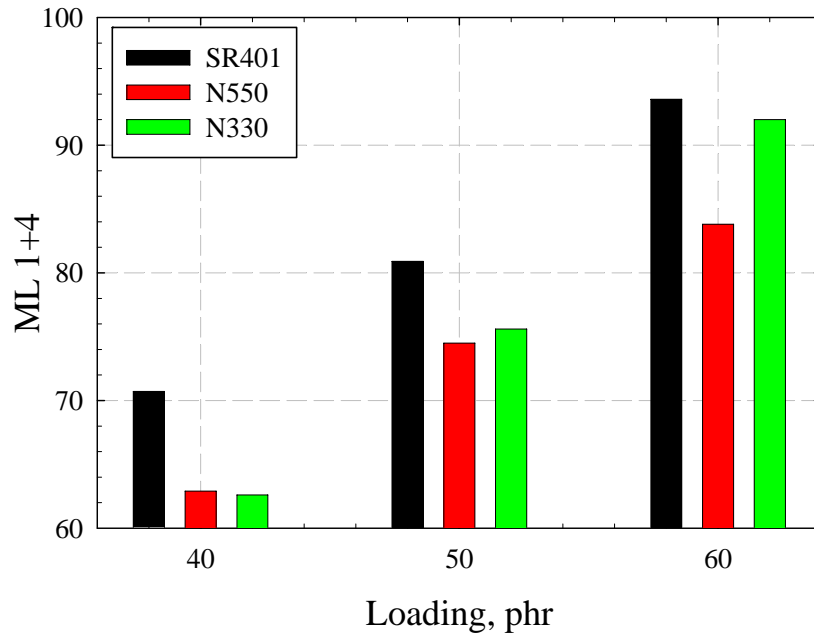


Figure 13. Mooney Viscosity for SR401 vs N550 and N330. Loading Study in Natural Rubber (Modified D3192)

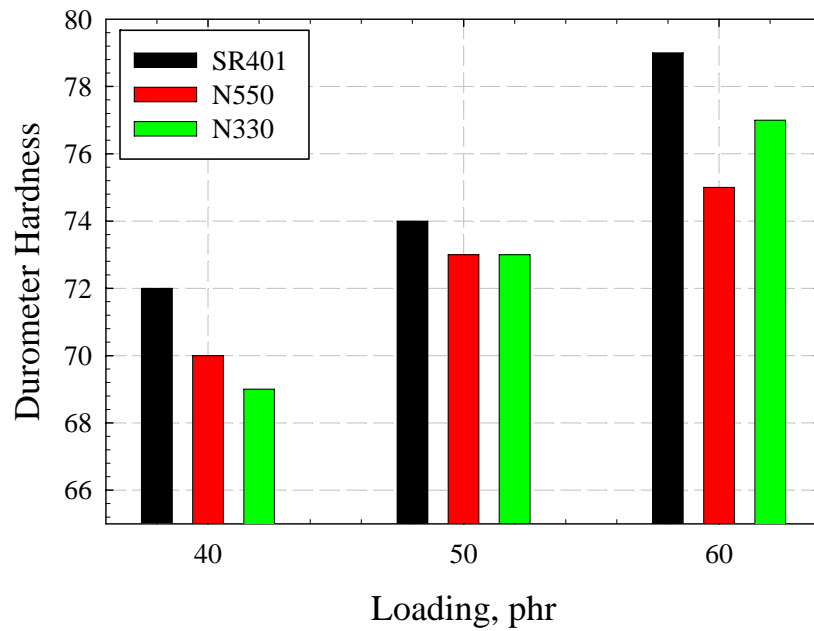


Figure 14. Durometer for SR401 vs N550 and N330. Loading Study in Natural Rubber (Modified D3192)

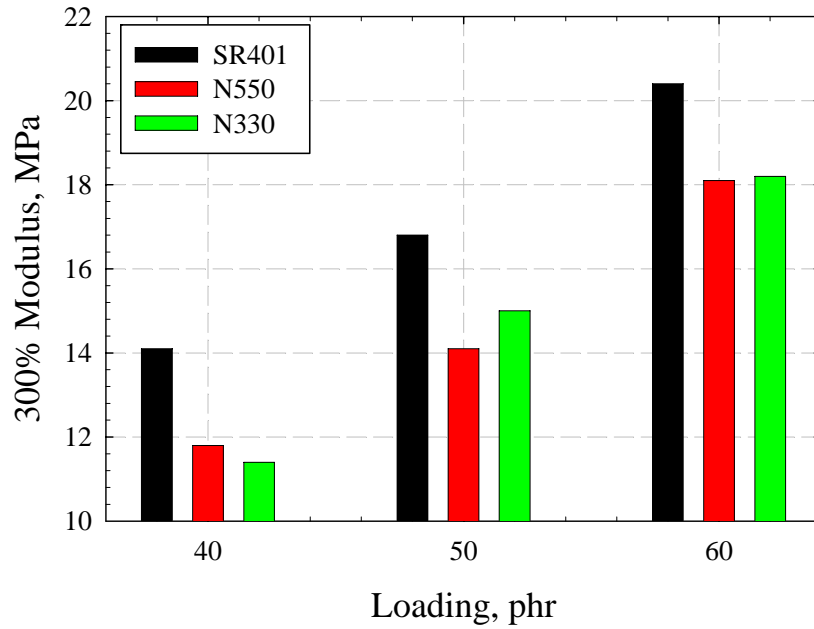


Figure 15. 300% Modulus for SR401 vs N550 and N330. Loading Study in Natural Rubber (Modified D3192)

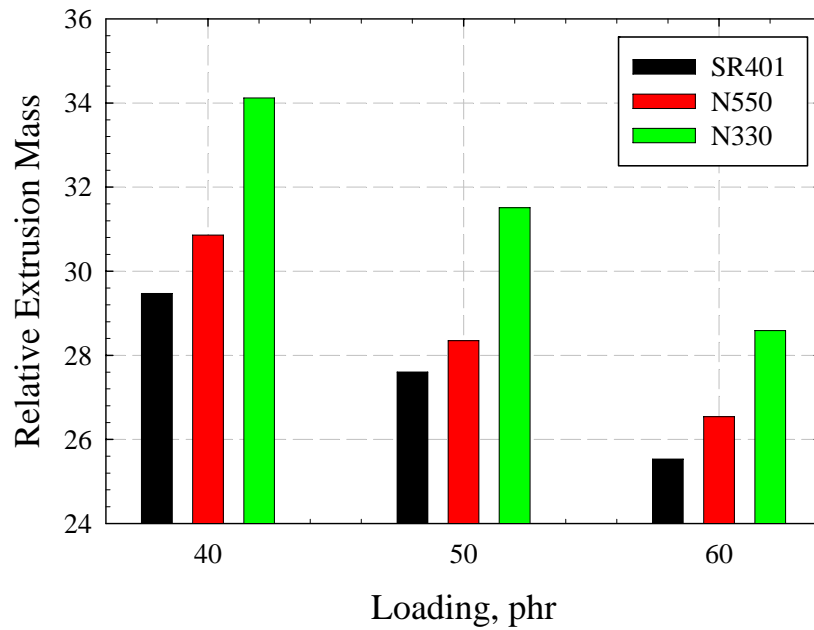


Figure 16. Relative Extrusion Mass for SR401 vs N550 and N330. Loading Study in Natural Rubber (Modified D3192)

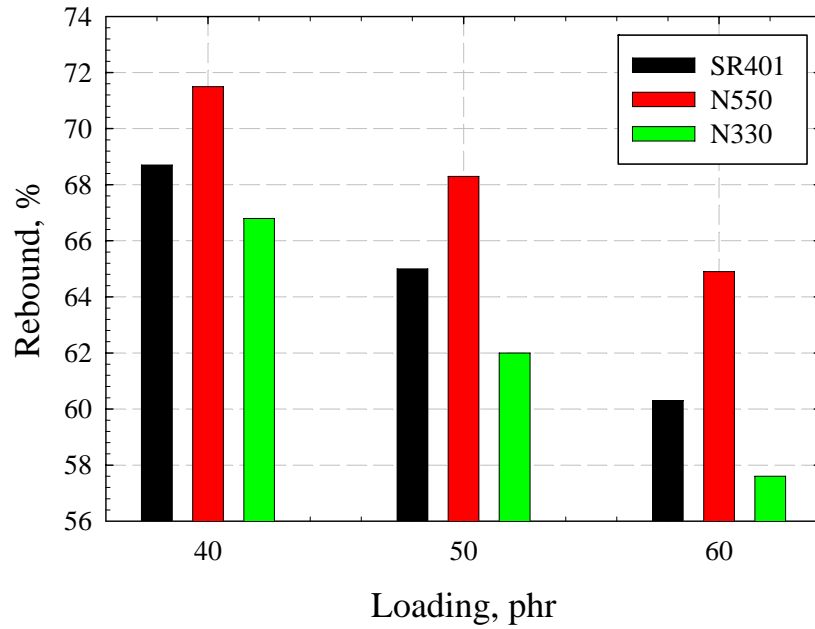


Figure 17. Rebound for SR401 vs N550 and N330. Loading Study in Natural Rubber (Modified D3192)

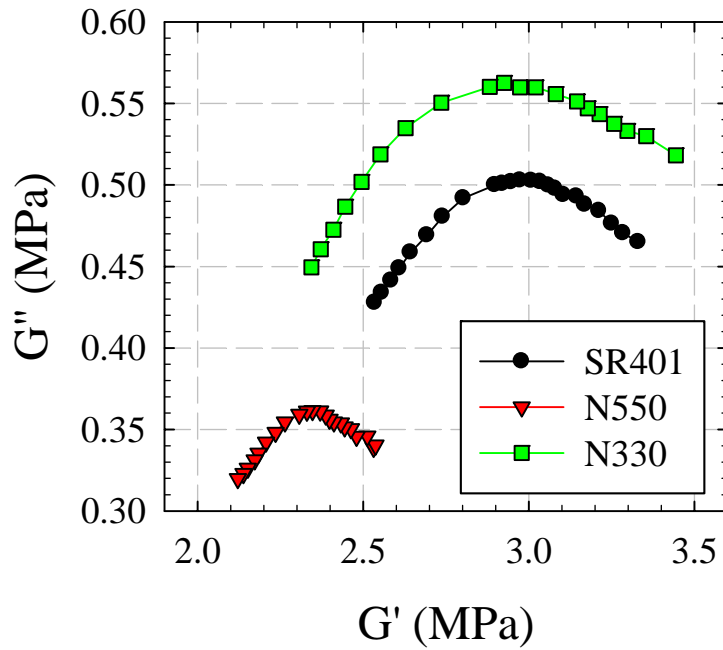


Figure 18. Low Strain Dynamic Properties for SR401 vs N550 and N330. Loading Study in Natural Rubber (Modified D3192).