

Technical

Material to give tire compounds lower density, lower hysteresis and improved wear

By Kurt Swogger
and August Krupp
Molecular Rebar Design L.L.C.

Molecular Rebar Design L.L.C. (MRD) has been developing a new form of commercially available multi-wall carbon nanotubes (MWCNTs) that result in dispersed individual, discrete, carbon nanotubes.

Recent developments have led to a rubber compound design that could address the tire performance needs for the premium tire segment, including the rapidly emerging electric vehicle market. Commercially supplied CNTs are delivered to MRD as micron-sized clusters of millions of nanotubes, which if mixed into rubber straightaway result in 20-50 micron-sized clumps in the elastomer compound.

TECHNICAL NOTEBOOK

Edited by John Dick

These clusters of nanotubes are difficult to properly disperse and thus do not result in the expected dramatic performance and physical property improvements as documented over the last 30 years. Differing from previous carbon nanotubes, MRD has invented and patented a composition that results in discrete and individual nanotubes within the elastomer compound, with no extra mixing processes or time. The resultant discrete nanotubes are branded as Molecular Rebar (MR), because they reinforce the compound on a nano-scale, similar to rebar in concrete only at the molecular scale.

Previously published studies, with results independently verified and tested by Akron Rubber Development Laboratory, among others, have demonstrated improvements in physical properties with a small usage of MR, less than 5 phr, usually 3 phr.¹⁻³ With this additive approach, MRD has been developing a customer base in high-value applications, both in parts, like oilfield blowout preventors, and in the tire market, like for off-the-road tread compounds. These applications are aimed at improved durability by improving wear, tear, cyclical fatigue, cut, chip and chunk properties by up to 75 percent.

Purpose and scope

Recently, adoption rates and production capacity increases have resulted in lowered raw materials costs of multi-wall carbon nanotubes. With this lower cost

Executive summary

Throughout the last 10 years, Molecular Rebar Design L.L.C., an Austin, Texas, company, has been developing a new form of commercially available multi-wall carbon nanotubes that result in dispersed individual, discrete, carbon nanotubes, marketed under the Molecular Rebar brand. Recent developments have led to rubber compound design that could address the tire performance needs for the premium tire segment, including the rapidly emerging electric vehicle market.

Molecular Rebar, in the newly developed third generation form, can be used to partially replace the carbon black in an off-the-road tire tread compound formula. This MRO Gen III material—when used at a replacement ratio of 3:8 for Molecular Rebar to N234 carbon black—can replace up to half of the typical carbon black content. This results in a compound that is lighter weight, has improved rolling resistance and heat build-up, and is significantly tougher, with greater cut and chip resistance.

Such improvements are expected to be useful in higher-performance tire applications, like electrical vehicles, OTR applications and luxury vehicle tires. The discrete carbon nanotubes allow greater freedom in performance properties to compound and tire engineers to re-write the boundaries of what is currently possible.

feedstock available today, MR can be economically sold at higher loadings for use in higher-priced premium tires. Because large quantities of discrete MWCNTs have not been used in rubber compounds previously, the resultant use-case scenarios and performance properties have not been evaluated. It is the purpose of this article to share the results of an investigation of the technical feasibility of replacing carbon black with higher quantities of MR, and to outline the new property relationships and performance boundaries. The targeted benefits for premium tire markets, including luxury SUVs and electric vehicles, include lighter weight tires with improved lower rolling resistance, heat buildup and toughness.

A previously studied OTR tread formulation will be used to evaluate property changes and new relationships, allowing for conclusive and statistically sound results. The scope of this experiment should encompass all carbon black-filled tread formulations, and the results should correlate to future formulation development in this sub-segment of tires.

Experimental design and techniques

Previously published results demonstrated the benefits of an “additive” approach in using Molecular Rebar in an OTR tread formulation. Those results will be repeated, along with the replacement of half of the existing N234 carbon black content.

Three formulas (Table 1) were produced using standard rubber compounding techniques: the control formula being the baseline compound being improved; +3MR -8CB using the MRO Gen II product in an additive fashion; and +12MR -33CB replacing approximately half of the existing

N234 carbon black content with Molecular Rebar, using the new MRO Gen III product.

The overall experiment was repeated twice to ensure consistency of results and to generate statistically sound data sets. Results reported in graph format are an average of those twice-tested results, with standard deviation represented by error bars.

Compounding technique

All formulations were mixed in a 1.6-liter Banbury-brand mixer in two passes. Before mixing, the Banbury was warmed up with a dummy batch of the base control formulation to 140°C (maximum allowed mixing temperature for this rubber formula in this study).

Pass 1 mixing includes rubber, carbon black and other chemicals, excluding the cure package. Temperature of the mix did not exceed 140°C. Mixing time was kept roughly to 6 minutes, with ~4 minutes of mixing taking place with downward ram pressure. The cure package was added in pass 2 and the maximum temperature was kept less than 105°C to avoid onset of sulfur crosslinking.

Both passes were flattened on an 18-inch, two-roll mill to ease processing and sample preparation. During two-roll mill calendaring, two flag-folds were performed during each pass to prevent anisotropy or alignment of fillers.

Rheology and curing kinetics testing

A Monsanto R100 single frequency oscillating die rheometer (ODR) was used to determine the optimum cure time (t90) at 150°C. Angular frequency of oscillation was set to 1 degree and time-of-data-gathering was set to 30 minutes.

Once both dies and rotors were preheated to 150°C and temperature stabilized, about 15g of material was cut from the pass 2 sheet and placed on the oscillating rotor; the dies were then closed. Scorch time (ts1), optimum cure time (t90), minimum (ML) and maximum (MH) torque were noted with the assistance of the ODR software as the vulcanization/crosslinking of the material completed.

Sample preparation technique

All test plaques of 150 mm x 150 mm x 2 mm dimensions were pressed using a heated compression press at 150°C and 45 tons of pressure for t90 + 2 minutes. Formulations were cured into wheels with dimensions of 51 mm diameter x 13 mm thick with a 13 mm diameter center hole using time t90 + 5 minutes for the respective sample.

Hardness testing

A Shore A hardness tester was used to determine an average Shore A hardness for each compound. The compounds were tested using the cured pucks on a solid surface, ensuring consistent values.

Fig. 1: Constrained tear test specimen.

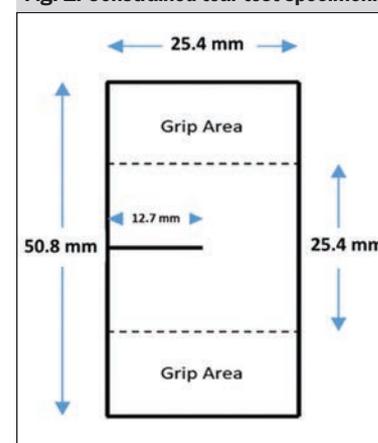


Table 2: ODR data, 150°C, 1° Arc.

	Control	+3MR -8CB (MRO Gen II)	+12MR -33CB (MRO Gen III)
ts1	05:07.4	05:20.7	06:19.8
t90	13:14.2	13:04.2	13:46.5
ML	8.03	8.38	11.56
MH	36.37	35.76	37.43
MH-ML	28.34	27.38	25.87

Table 3: Average Shore A hardness.

	Control	+3MR -8CB (MRO Gen II)	+12MR -33CB (MRO Gen III)
Hardness	69.67	69	67.5

Table 1: Experimental formulations.

Material	Control Formula	+3MR -8CB (MRO Gen II)	+12MR -33CB (MRO Gen III)
	PHR	PHR	PHR
Natural Rubber- CV60	70	70	70
PBR- Cisamer 1220	30	30	30
50:50 MRO Gen II- Naphth		6	
60:40 MRO Gen III- Naphth			20
Carbon Black N234	65	57	32
HyPrene 150 Naphthenic Oil	15	12	7
Zinc Oxide	4	4	4
Stearic Acid	3	3	3
Antioxidant 6PPD	2.5	2.5	2.5
Microcrystalline Wax	2	2	2
Accelerator TBBS	1	1	1
Sulfur	1.5	1.5	1.5

The authors

Kurt Swogger is the CEO and a founding member of Molecular Rebar Design L.L.C.

He began his career at Dow Chemical Co. in 1972. While there, he held positions in research, manufacturing and marketing in the Ag Chemicals, Consumer Products, and Polyolefins businesses. In 2003, he was appointed vice president of plastics research and development, and was responsible for polyethylene, polystyrene, automotive, engineering plastics, building and construction products, rubber and thermosets. In 2005, he was named R&D vice president for the Performance Plastics and Chemicals businesses. He also served on the board of directors for Univation, a joint venture between Dow and Exxon. Swogger retired from Dow in 2007.

He received his bachelor's in chemical engineering from Case Western Reserve University and is a registered professional engineer in Texas. Swogger currently is on the Industrial Advisory Board for the Academies of Medicine, Engineering and Science of Texas, the Texas A&M Energy Institute, the Plastics Pioneers and the Case Western Reserve Visiting Committee.

August Krupp is director of rubber development at Molecular Rebar Design. He has a degree in applied science-mechanical engineering from Washington University in St. Louis. He is co-inventor on many of the patents covering Molecular Rebar products for rubber and the resultant compositions.

Krupp helped restart the elastomer project in 2016 after previously completing an internship at MRD, and has been instrumental in developing MRO products, the associated go-to-market strategy, and ensuring key relationships with customers. He is widely published and has given presentations for authored papers at the ACS Rubber Division's International Elastomer Conference.



Swogger



Krupp

Technical

Tensile testing

Tensile testing was performed according to ASTM D412-16 using an Instron 3360. The die used to create the tensile specimens was DIN-53504-S2. Five specimens were produced from each formulation to be tested. Tear testing was performed by using two methods. One is a Die C test according to ASTM D 624, and the second one is a lab-based, single-edge notch constrained tear.

A pull rate of 500 mm/min is used for the constrained tear test. Tear samples were die-cut, making a rectangle 50.8 mm x 25.4 mm. A slice perpendicular to the side of the specimen was also made during die cutting. A total of five specimens were tested per sample compound. A typical single-edge notch test specimen with dimensions is shown in Fig. 1.

Cut and chip testing

Cut and chip resistance of the cured formulations was performed using a Montech CC3000. The specimens were rolled at 1,080 RPM and the frequency of the impacting blade was set to 30 Hz. Time of the test was 5 minutes. Mass and diameter loss measurements were taken after the test time. Cut and chip resistance was calculated as a reciprocal of volume loss, calculated from the theoretical density and resulting mass loss.

Dynamic mechanical analysis testing

Dynamic properties of cured slab strips measuring 8 mm x 4 mm x 2 mm are performed using a TA Instruments DMA Q800.

Strain sweep tests are carried out from 0.1 percent to 30 percent strain in tension mode (0.01N preload and 1Hz frequency) at three different temperatures: See **Compounds**, page 18

Fig. 2: Tensile test data for experimental compounds, strength 100, 200 and 300 percent modulus.

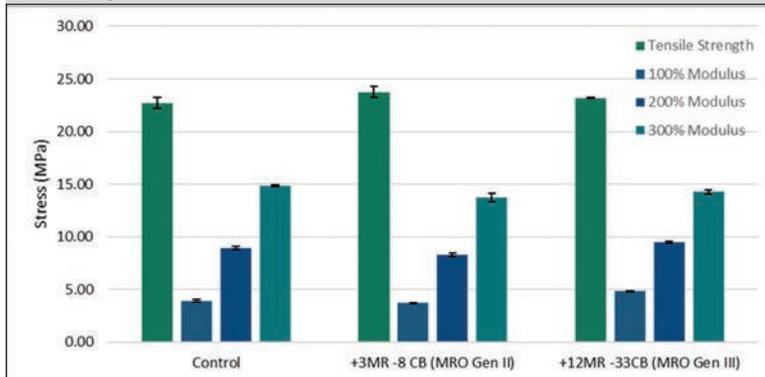


Fig. 3: Constrained tear test data, maximum stress.

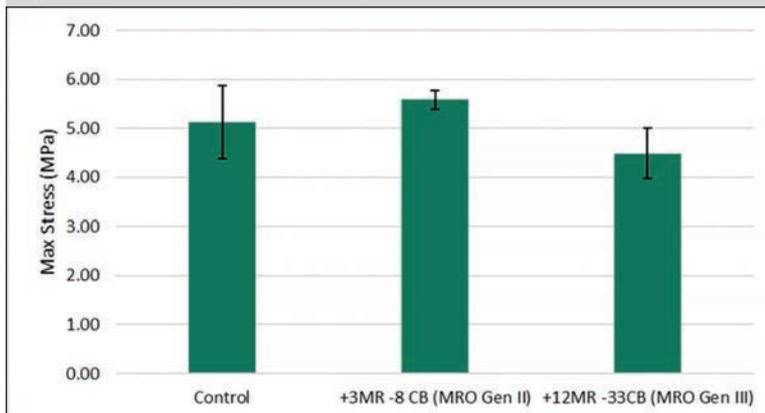


Fig. 4: Die C tear test data, max load per thickness.

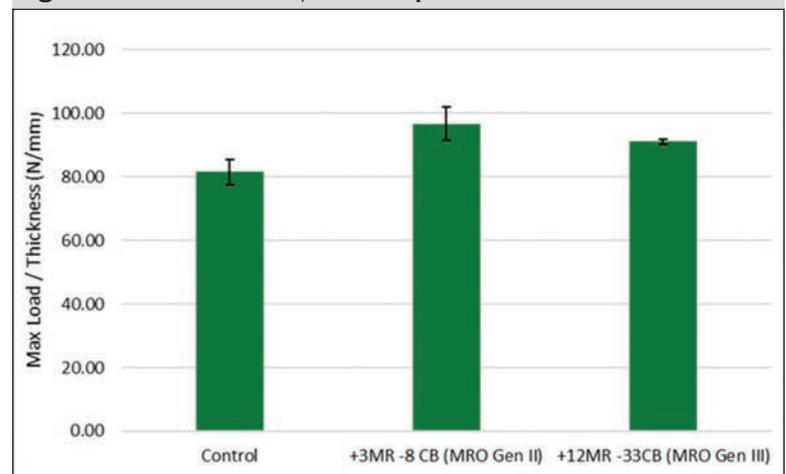
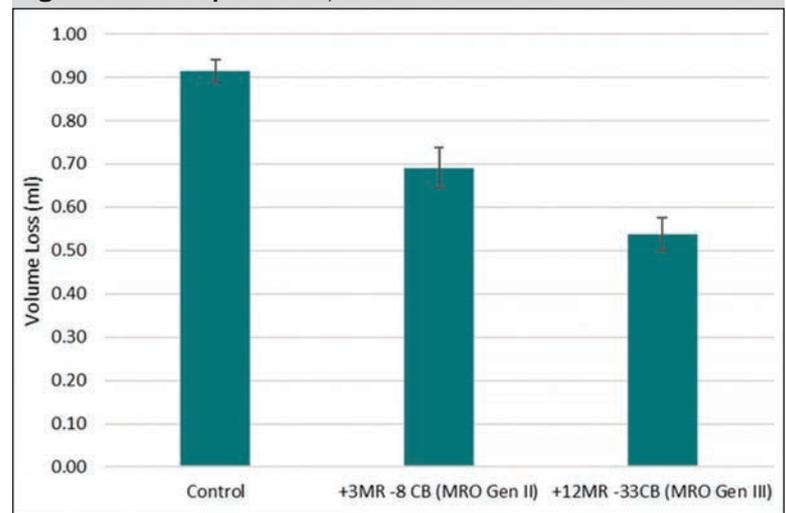


Fig. 5: Cut and chip test data, volume loss in ml.



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China's Zhonghui to build conveyor belt plant

By Jane Ho
European Rubber Journal

WUHU, Anhui—Zhonghui Rubber Technology signed a contract March 17 to build a \$76 million agricultural machinery belt plant in Wuhu, which is in the Anhui province.

Located in the city's Sanshan Economic Zone, the project will have an annual capacity of 80 million meters of high performance conveyor belts

for agricultural machinery and 30,000 metric tons of rubber track, the Wuhu government said.

Smart manufacturing technology will be used in the project, which will create 400 jobs when in full operation, and generate \$91 million in annual sales, the government said.

Zhonghui is headquartered in Wuxi, Jiangsu province, and also makes rubber belts for engineering

machinery and the auto sector. Its products are marketed under the brand name Zhongliang and are exported to Europe, the U.S. and Southeast Asia.

The company posted annual sales of \$46 million last year, and supplies international agricultural machinery brands such as Kubota and Zoomlion as well as other local Chinese manufacturers.



Zhonghui Rubber Technology is spending \$76 million to expand in China.

Technical Compounds

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0°C, 60°C and 100°C.

The ratio of loss modulus to storage modulus, value $\tan \delta$, is observed at 10 percent strain for each of these temperatures. $\tan \delta$ at 0°C relates to wet grip (WG), $\tan \delta$ at 60°C relates to the rolling resistance (RR) and at 100°C correlates to heat build-up (HBU).⁴

For an improved tread compound, both values at 60°C and 100°C should be lower than the control, correlating to less energy loss and improved rolling resistance and heat build-up properties, respectively. $\tan \delta$ at 0°C should be the same or higher for an improved compound, representing the same or improved wet grip properties.

Results

Curing rheology and kinetics data are shown in **Table 2**. No major differences are seen between the control and MRO Gen II samples, while the half replacement formula utilizing MRO Gen III has both a higher ML and MH value, and a smaller difference between the two. This could represent slightly less stiffening effect contribution from the curing package, and more reinforcement contribution from the filler itself. The increase in ML of ~40 percent could cause processing issues and

needs further evaluation.

Shore A hardness values are shown in **Table 3**. Using MRO Gen II as an additive results in a very similar hardness value, while replacing half of the carbon black with MRO Gen III softens the cured compound slightly.

Tensile test values can be seen in **Fig. 2**, where the ultimate tensile strength, 100 percent modulus, 200 percent modulus, and 300 percent modulus are shown for each compound.

A constrained tear test was used to measure maximum stress during tear propagation, resulting in **Fig. 3**. Because of the natural rubber content in the compound, tear tests have some standard deviation, making a conclusive statement on performance difficult.

The Die C tear test was used to measure maximum load per unit thickness in N/mm during tear initiation, resulting in **Fig. 4**. The data on this tear test is more consistent than the constrained tear test and shows a small improvement in this tear resistance with the addition of either MRO Gen II as an additive or MRO Gen III as a carbon black replacement.

The cut and chip test is a reasonable indicator of macro-abrasive wear resistance, as previously reported by other authors.^{5,6} Both samples with MR products demonstrated greatly improved cut and chip resistance, with the

additive MRO Gen II sample achieving 24 percent improvement and the replacement MRO Gen III sample showing 40 percent improvement, as shown in **Fig. 5**. The improved macro-abrasive wear resistance is likely correlated to the above improvements in tear resistance.⁷

Rolling resistance ($\tan \delta$ at 60°C) and heat build-up ($\tan \delta$ at 100°C) correlations as tested by DMA at 10 percent strain are shown in **Fig. 6**. A small improvement of 2 percent and 5 percent in rolling resistance is demonstrated for both the additive MRO Gen II and replacement MRO Gen III sample, respectively.

The trend is flattened for the heat build-up indicator, with the MRO Gen II sample having a 1 percent improvement and the MRO Gen III replacement sample being equivalent to the control. It is supposed that the overall reduced content of reinforcing filler, although having similar total surface area and thus bound rubber content, results in less filler-filler interaction.

Based on previously published studies, this filler-filler interaction is the primary component of Payne Effect and hysteretic losses.^{8,9} By reducing overall quantity of reinforcing carbonaceous material, those hysteretic losses can be lowered, even though wear resistant properties are improved.

Wet grip ($\tan \delta$ at 0°C) correlations as tested by DMA at 10 percent strain are shown in **Fig. 7**. Both samples utilizing MR for reinforcement are slightly worse than the control sample, showing a detrimental wet grip effect of 3 percent and 8 percent for Gen II and Gen III, respectively. It is hypothesized that the increased volume content of elastomer components causes

$\tan \delta$ at 10 percent strain to decrease, a known effect that aligns with previously reported trend data by other authors.¹⁰

In future work, there will be efforts to offset this detrimental effect by changing the polymer composition of such a compound, such as adding styrene butadiene without sacrificing wear resistance, as wear resistance is improved with the Molecular Rebar MWCNTs.

It should be noted that with the reduction in total loading of reinforcing carbon content, the density of the produced compounds decreases, as shown in **Table 4**. Weight savings of 1 percent with additive Gen II usage and 4 percent with replacement Gen III is expected to be beneficial for uses seeking lighter weight tires. With even further reductions in carbon black content planned, future compounds could be up to 10 percent lighter in total.

Summary and conclusion

Multi-wall carbon nanotubes in a discrete form, known as Molecular Rebar, can provide benefits to dynamic properties and wear-resistant properties simultaneously when used as a replacement for existing reinforcing carbon black content. Third generation MR was delivered in an oil form, called MRO Gen III, using commercial mixing techniques to a known OTR tread formulation. MRO Gen III was used to replace half of the existing N234 carbon black content with only three-eighths the quantity of MWCNTs. Summarized results of the three compounds tested are shown in **Fig. 8**.

Using MRO Gen III to replace part of the carbon black results in a compound that is 4 percent less dense, has 5 percent improved roll-

ing resistance, and is 40 percent more resistant to cut and chip abrasion. By having a more reinforcing rod-like filler in the form of individual MWCNTs replace a less reinforcing spherical filler like N234 carbon black, wear resistance can be improved, bulk physicals like modulus and hardness can be maintained, and dynamic properties can be improved. Two points on the "magic triangle" of rubber compounds can be simultaneously improved in a commercially applicable fashion.

With further development, it is expected that these improvements will be useful in many high-performance markets, such as OTR tires, EV tires, and luxury vehicle segments. Future work will adjust formulations to compensate for detrimental wet grip properties as needed, and will explore new limits of the Molecular Rebar technology.

By decreasing density, lowering rolling resistance, and improving wear resistance, Molecular Rebar can help expand the envelope of tire design with improved materials science. These combinations of properties allow greater freedom to tire design engineers, whether it be further light-weighting via decreased tread thickness, improved tread designs sacrificing some cut and chip resistance, or longer-lasting more fuel-efficient tires for tough applications.

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Fig. 6: DMA data, $\tan \delta$ at 60°C and 100°C.

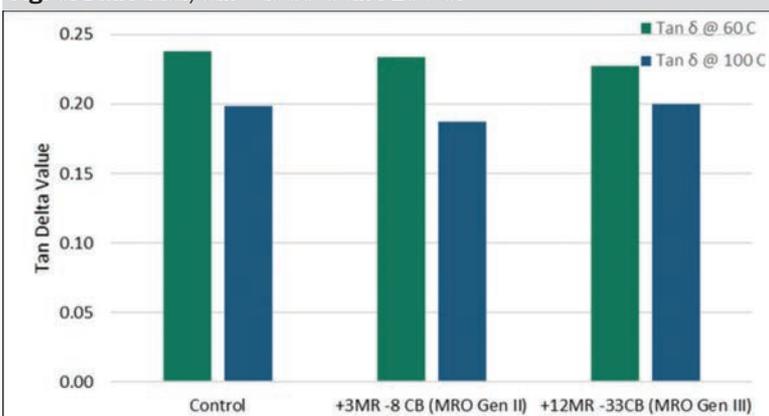


Fig. 7: DMA data, $\tan \delta$ at 0°C.

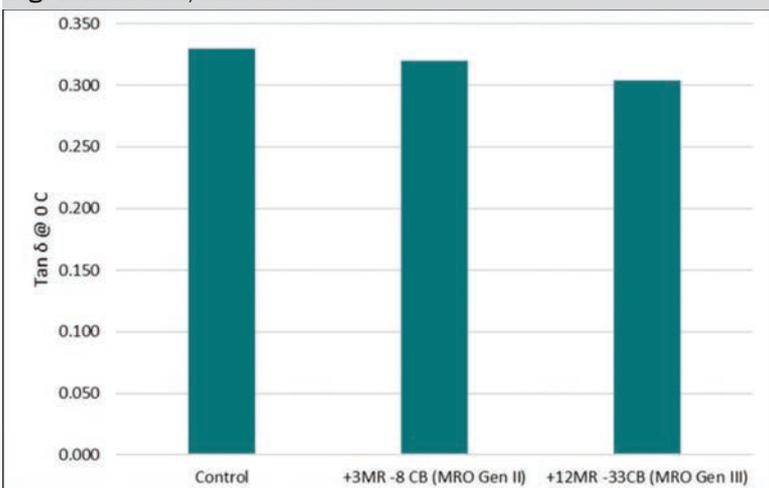


Table 4: Theoretical density of compounds.

	Control	+3MR -8CB (MRO Gen II)	+12MR -33CB (MRO Gen III)
Specific Gravity	1.16	1.147	1.112

Fig. 8: Summarized critical data.

