From low-cis to high-cis, to high vinyl architecture: an insight into polybutadiene rubber

By Federico S. Grasso, Fabio Bacchelli and Salvatore Coppola
Versalis S.p.A. (Eni)

Executive summary

Butadiene rubber (BR) is commercially available in two main forms. One contains 1,4-cis repeating unit levels at around 40 percent, which is called low-cis BR. And the other with levels that range from 92-98 percent, called high-cis BR.

Moreover, high-vinyl polybutadienes may be obtained, which contain pendent vinyl groups as a result of 1,2-polymerization mechanisms. These rubbers had properties similar to those of SBR and are used with a specific compounding strategy.

This paper reports an overview of several different polybutadienes with different molecular architecture and related property-structure relationships. Functionalization, being a chemical parameter, is not taken into account. In addition, besides traditional BR grades, new Nd-based polybutadienes containing a specially designed molecular architecture are introduced, to optimize processing and performance at the same time.

The molecular architecture able to conjugate those extremely different aspects is discussed on the basis of the linear viscoelastic response. By considering various recipes, advantages in extrusion behavior and hysteresis are addressed together with commonly used testing parameters.

Polybutadiene rubber (BR) is the second largest synthetic rubber produced, next to SBR. Currently, tires are the primary application for BR, while other segments include plastics modification, footwear, technical goods and golf balls.

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Butadiene may be present in polymer macromolecules in the form of cis-1,4, trans-1,4 and 1,2 structural units with pendant vinyl groups. The content of individual forms of butadiene structural units in polymeric chains depends on the polymerization method, and it determines the basic properties of BR, which is commercially available in two main forms. One containing 1,4-cis repeating unit levels around 40 percent is called low-cis BR, and one with levels that range from 91 to 98 percent is called high-cis BR.

The demand for these two products, each with their own distinct properties, comes from major consumption segments such as tires and retreading, with high-cis-BR being the most appropriate for these applications. Vulcanized high-cis BR presents high elasticity and resilience, low heat build-up, high resistance to abrasion and to cut growth, good flexibility in low temperatures, and high fatigue cracking resistance. This set of properties makes high-cis BR an excellent elastomer for the tire industry.

On the other hand, its compositions do have low skidding resistance and low resistance to heat and ozone and, in particular, it is considered a rather difficult polymer to process. Four different technologies with Ziegler–Natta catalysts can be used in the commercial production of BR with high 1,4-cis repeating unit levels: titanium (Ti), cobalt (Co), nickel (Ni), and neodymium (Nd). The higher polydispersity and branching content found in the BR–Ni and BR–Co systems make polymer processing easier in relation to the more linear polymers obtained by neodymium catalyst.

But these same characteristics, which facilitated processing, influence in a negative way the mechanical properties of the compositions prepared from such polymers. The physical and rheological properties are dictated by controlling the polymer structure. Highly linear neodymium-polybutadiene with a narrow molecular weight distribution is desirable for high abrasion resistance, low heat build-up and high tensile properties. Although linear and ultra-high cis polybutadiene possesses high compound viscosity, the disadvantage can be reduced by introducing a branched structure.[1,2]

Experimental

Polybutadiene samples used in this work are Europrene and Intene commercial grades from Versalis. The main properties are summarized in **Table 1**. The linear viscoelastic behavior of the raw polymers is obtained through frequency sweep test in SAOS test conditions and torsional mode (the reference temperature is 110°C).

During the test, strain is controlled in order to respect the linear viscoelastic regime of the material. Frequency sweep data are extended at very low frequency by applying creep/recovery test in the SAOS regime. Creep/recovery data are converted into dynamic moduli by means of the Schwarzl relationships.[3]

Compounding was carried out using laboratory internal mixers with Banbury rotors. Physical and mechanical properties of rubber compounds were measured according to ASTM, DIN or ISO standards. The Rolling Resistance Index on vulcanized specimens was determined through strain sweep measurements using a torsional bar (5-percent strain, 10 Hz, 60°C). Temperature sweep tests on vulcanized specimens were carried out with torsional bar geometry at 1 Hz and 2°C/min.

Results and discussion

Low-cis BR

In **Table 1,** several Versalis commercial BR grades are listed. Intene materials are obtained by a continuous polymerization process, using Lithium catalyst, whereas Neocis BR40 is polymerized by a continuous solution process using a Neodymium catalyst. The Intene series represents low-cis materials, all having cis content of about 38 percent and vinyl content of about 10 percent, and varying Mooney viscosity.

All low-cis polymers have a prominent linear molecular architecture and narrow molecular weight distribution, with the exception of Intene C30, which is a mixture of linear and star-branched polymer chains. Neocis BR 40 is a traditional Nd-BR grade, which we introduce here for comparison with low-cis BR. As well known in the industrial practice, low-cis BR is widely used in rubber applications due to its peculiarity of providing excellent compoundability and processability.

In **Fig. 1** we show compounds at discharge after a 1.5 minute mixing duration step that we carried out in a laboratory tangential mixer (1.5 liters). We observe that the compound aspect is noticeably different if we use Intene C30 (left) or Neocis BR40 (right). More precisely, the Neocis BR40-based compound still appears unfinished, as the carbon black is not properly incorporat-

Table 1: Properties of Versalis commercial polybutadienes: Europrene series (Neocis and BR HV80) and Intene series. Mooney and Tg data refer to measured values.

	Mooney, MU	Vinyl, %	Cis, %	Tg, °C	Polymer structure	MwD
INTENE 30	30	low	low	-93	Linear	Narrow
INTENE 40	37	low	low	-93	Linear	Narrow
INTENE C30	46	low	low	-94	Star branched	Narrow
INTENE 50	48	low	low	-93	Linear	Narrow
INTENE 60	68	low	low	-93	Linear	Narrow
BR HV80	70	high	low	-31	Highly linear	Narrow
Neocis BR40	43	negligible	high	-107	Mainly Linear	Broad
Neocis BR45EP	44	negligible	high	-107	Optimized	Narrow
Neocis BR60	63	negligible	high	-107	Mainly Linear	Broad
Neocis BR61EP	60	negligible	high	-107	Optimized	Narrow

Fig. 1: Compound aspect at mixer discharge. Mixing duration is 1.5 minutes. Low-cis BR (Intene C30, left) and high-cis BR (Neocis BR40, right) are the investigated materials. The adopted compound formulation is a chafer compound (BR/NR 70/30, 70 phr of N375).

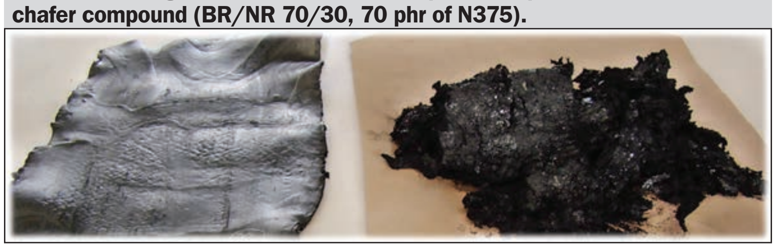
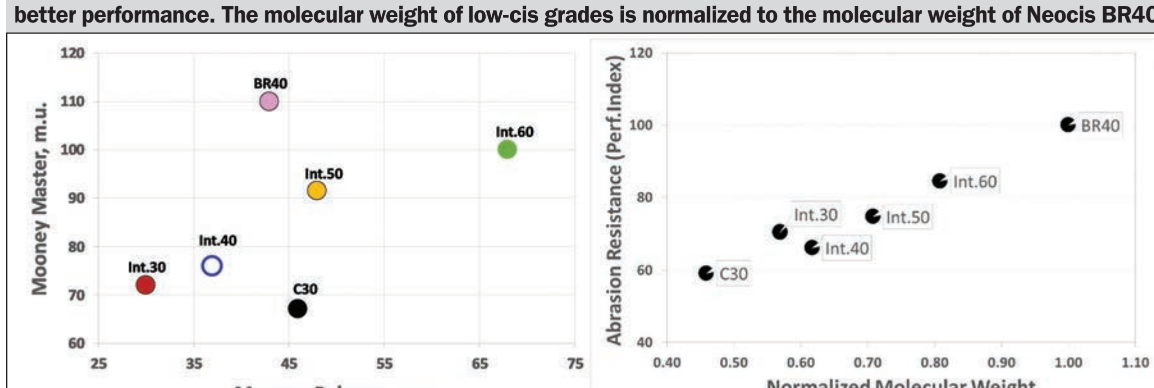


Table 2: Comparative laboratory test for chafer compound (BR/NR 70/30, 70 phr of carbon black N375). A) Low-cis BR (Intene C30), B) High-cis-BR (Neocis BR40).

a) low-cis BR (Intene C30)	1:30 min	3:00 min	6:00 min
Garvey Index (120°C, 60rpm)	16	16	16
TS (MPa)	19.2	20.0	19.6
Abrasion (mm3)	70	67	66
HBU (°C)	55	55	54

b) High-cis BR (Neocis BR40)	1:30 min	3:00 min	6:00 min
Garvey Index (120°C, 60rpm)	-	11	15
TS (MPa)	-	18.2	19.8
Abrasion (mm3)	-	50	48
HBU (°C)	-	47	46

Fig. 2: Comparative tests of low-cis BR grades (Intene) vs. high-cis BR (Neocis BR40) in high abrasion resistance formulation. Polymer ratio is BR/NR=75/25; filler loading is 75 phr of N234. Mixing is performed in two stages in a laboratory Banbury mixer; the overall mixing time is six minutes. Masterbatch Mooney vs. raw polymer Mooney is shown on the left. The abrasion resistance index is shown as a function of the polymer's average molecular weight on the right. This index is calculated assuming Neocis BR40 as reference (value is 100) so that higher value means better performance. The molecular weight of low-cis grades is normalized to the molecular weight of Neocis BR40.



The authors

Fabio Bacchelli received his doctorate in chemical engineering from the University of Bologna, Italy. He began working as a process engineer at Versalis S.p.A., where he also has been leading the research and development department for the Elastomer Physics and Elastomer Processing unit.


Bacchelli

Bacchelli is head of technical management of SBR/BR/Latex in the Elastomer Business Unit. He also is a member of the Scientific Council of the German Institute of Rubber Technology.

Federico Grasso got his master's in mechanical engineering from the University of Catania, Italy. He has been working in the Elastomer Physics Department of Versalis R&D and is technical manager for tire applications in the Elastomer Business Unit.


Grasso

Salvatore Coppola got his doctorate in chemical engineering from the University of Napoli Federico II in Italy. He joined Versalis R&D as a scientist and currently is head of the Department of Elastomer Physics.


Coppola

ed and finely dispersed in the polymer matrix.

Such an experiment is specifically carried out to reveal Intene C30's high inclination to the compounding phase, even in severe mixing conditions (short mixing times in combination with high filler loading). Such inclination arises from Intene C30's peculiar combination of linear and star-branched molecular architecture.

In **Table 2** we show the results of the lab experiment where, for the same compound recipe as above, we increase the mixing time in steps from 1.5 minutes to six minutes. The experiment confirms that high-cis Neocis BR40 requires longer mixing times than low-cis Intene C30. In fact, with optimal mixing conditions, the compound based on Neocis BR40 can achieve very competitive performances, even being superior to Intene C30 in terms of mechanical properties and reduced energy dissipation (heat build-up is shown). The better extrudability of Intene C30 remains confirmed, as shown by the Garvey test.

In **Fig. 2** (left) we further extend the comparison between low-cis and high-cis BR to all the investigated low-cis grades. The polymeric blend ratio is kept similar to the above-mentioned experiments, but filler type and loading level are different, as the high abrasion resistance recipe was adopted to further stress on the differences between material grades. Also in **Fig. 2** (left), the compound before the addition of the curing agent is referred to as masterbatch compound. We observe that masterbatch Mooney viscosity depends on the Mooney viscosity of the raw polymer, with the exception of Intene C30 and Neocis BR40, which are bottom low and top high values in the masterbatch Mooney raking, respectively.

This result meets our expectations and is not further commented as already discussed above. This experimental lab trial confirms the superior mechanical performances of high-cis BR (Neocis BR40) with respect to the low-cis BR (Intene) series.

In **Fig. 2** (right), for readability purpose we only show the results of abrasion resistance, which is the most important parameter, as this formulation is meant for high abrasion resistance applications. It is interesting to observe that the abrasion resistance index shows linear trend with respect to the average molecular weight of the raw polymer. We selected Intene 50 and Intene C30 with comparable Mooney viscosities; we observe differences in the compound properties, due to their different molecular architectures (partially star-branched vs. fully linear structure).

In **Fig. 3** we show the dynamic-mechanical loss tangent curves as a function of temperature. All plots show two distinct peaks, one of which always occurs at around -55°C, while the other can be located at either -75°C or -90°C, depending on the BR type. The presence of two peaks in the compound indicates the immiscibility between the NR and the BR phases, with the local maxima being ruled by the transition glass temperature values of the raw materials.

Focusing on the local maxima of loss tangent curves, compounds show peaks with different heights, thus suggesting different filler distribution[10] and filler dispersion[11] within the NR/BR phases. To further explore this point, in **Fig. 4** we show the values of the loss tangent peak related to the BR phase as a function of the normalized molecular weight of the raw polymers. We observe a good correlation for the Intene grades, while instead the high-cis BR grade (Neocis BR40) does not fit the trend. This result is somehow expected, as it is known from the literature[12] that high-cis BR can experience crystallization at temperatures near or below 0°C, and that the crystallization strongly affects the viscoelastic response of the raw material, in terms of loss tangent and moduli.[13]

As a consequence, the value of the Neocis BR40-phase peak in **Figs. 3 and 4** cannot be directly compared with the values of Intene grades. An additional indication of this crystallization effect occurring in Neocis BR40 can be found again in **Fig. 3**, where the local maximum of the NR phase is located at lower position for the Neocis BR40-based compound curve. This suggests that higher filler incorporation occurs in the NR phase when Neocis BR40 is used in the compound in place of Intene grades, so the Neocis BR40 phase peak would be reasonably expected to be higher unless crystallization is taken into account.

High-vinyl BR

After discussing low-cis BR polymers in comparison with high-cis BR, we provide an insight into the BR HV80 Versalis commercial grade. The latter is a solution polymerized high vinyl butadiene polymer produced by continuous process using a lithium catalyst.[4,5]

BR HV80 has a vinyl content of around 77 percent, comparable to that of high vinyl SSBR. High-vinyl BR can be used in compound applications requiring specific performances at low temperature. As an example, we refer to SSBR/BR/NR compounds for winter tread with polymer ratios of 55/40/20 respectively.

SSBR is a continuous high-vinyl SSBR (SOL R C2564T, TDAE extended, styrene 25 percent (w/w) over total chain units and vinyl 64 percent (w/w) over butadiene chain units.

The adopted BR type is Neocis BR40, while filler is precipitated silica in a content of 95 phr. BR HV80, introduced in partial replacement of the SSBR (20 phr), is able to improve the loss tangent curve in the range from -30°C to +20°C (**Fig. 5**). Data in **Table 3** shows that lower values of the complex dynamic modulus (G*) are found in the same temperature range. High-vinyl BR, when properly formulated, brings about improvement in the ice skid resistance, wet grip and rolling resistance indexes at the same time.

Fig. 3: Dynamic-mechanical curves of BR/NR cured compounds are shown. Details about mixing conditions and compound recipe are available in Fig. 2. Measurements are carried out in torsion at low deformation level (strain=0.1%) and 1Hz frequency.

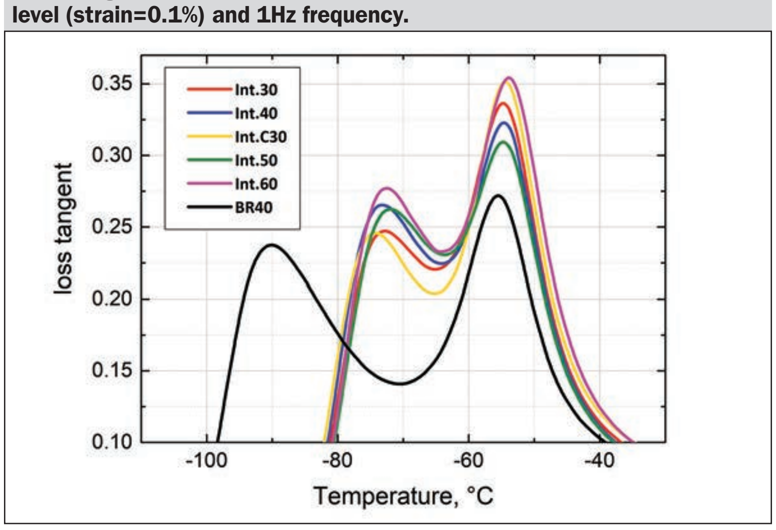
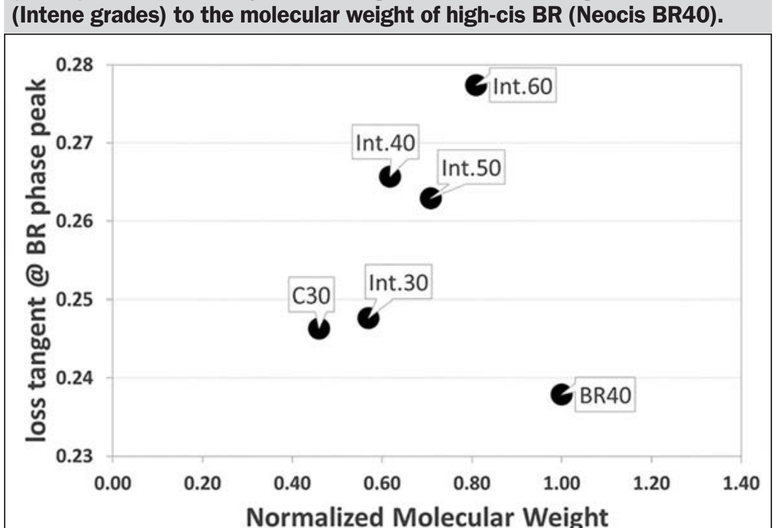


Fig. 4: The values of the loss tangent are taken at the local maxima (y-axis), which is related to the BR-phase (peaks occurring in the curves at lower temperature values, see Fig. 3). The normalized molecular weight (x-axis) is calculated by normalizing the molecular weight of low-cis BR (Intene grades) to the molecular weight of high-cis BR (Neocis BR40).



High-cis BR

Four different technologies with Ziegler–Natta catalysts can be used in the commercial production of BR with high 1,4-cis repeating unit levels: titanium (Ti), cobalt (Co), nickel (Ni), and neodymium (Nd). Depending on the type of catalyst, different molecular architectures are achieved, with different molecular weight distributions as well as different branching levels. In **Fig. 6**, a qualitative schematic of branching levels vs. catalyst type is shown.

High-cis Nd-BR is known to be a high performing, very elastic polymer. However, processing may become challenging, as seen for example in rough extrudates. The higher polydispersity and branching content typical of Ni-BR and Co-BR make polymer processing easier in relation to the more linear architecture obtained by neodymium catalyst. On the other hand, these same characteristics, which facilitated processing, influence in a negative way the vulcanizate properties of the compositions prepared from such polymers.

Table 4 summarizes literature data,[1] providing a qualitative insight into major advantages/disadvantages of different high-cis BR types in two different carbon black-based compound formulations. Nd-BR clearly provides excellent mechanical properties as well as low levels of hysteresis for the cured compounds, due to molecular patterns featuring higher linearity.

To further investigate differences, we have considered and

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Fig. 5: Dynamic-mechanical curves of SSBR/BR/NR compounds for winter tread and polymer ratio of 55/40/20, respectively. SSBR is a TDAE oil-extended grade polymerized in continuous process and having styrene/vinyl composition of 25/64 percent in weight. The adopted BR type is Neocis BR40, while filler is precipitated silica in a content of 95 phr. High vinyl BR (BR HV80) is introduced in partial replacement of the SSBR, in maximum amount of 20 phr. In the plot, the loss tangent curves of cured compounds with and without BR HV80 are shown.

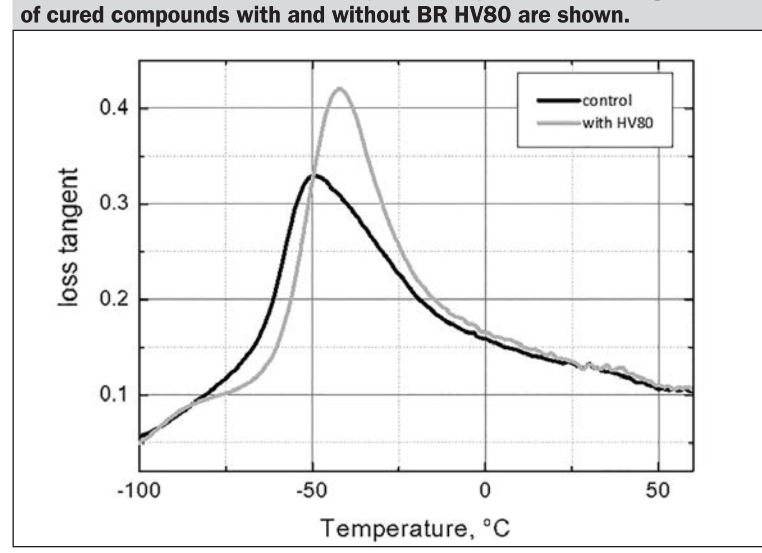

Table 3: Tire predictors for winter tread SBR/BR/NR silica compound. The introduction of high-vinyl BR (BR HV80) in partial replacement of SSBR brings about improvement of the major dynamic properties. Values are indexed so that higher values mean better performance.

Indexed property (higher is better)	Control SSBR	SSBR/HV80
Ice Skid Index (G*@ -20°C)	100	133
Wet Grip Index (tanδ @0 °C)	100	104
Rolling Resistance Index (tanδ @60 °C, 5% strain)	100	110

Fig. 6: Schematic chart of high-cis BR grades using different catalytic systems. Comparison is limited to the catalysts typical of industrial polymerization processes.

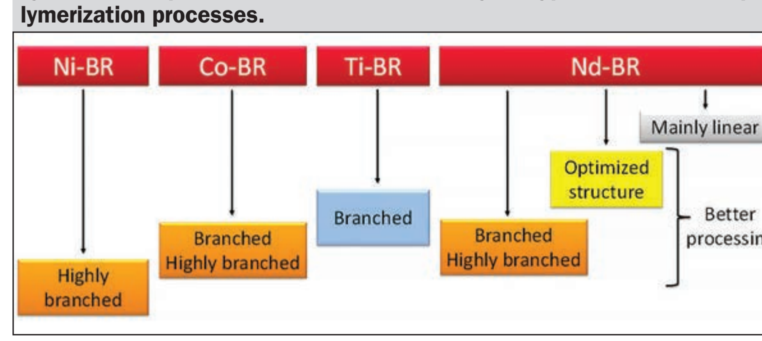

Table 4: Different high-cis-BR types are tested in carbon black-based compound recipes. Comparative data are shown in terms of qualitative ranking, by using digits from 1 to 3, being the best and the worst performances, respectively. Such typical data, that we have re-elaborated, are taken from the literature.[1]

Property, ASTM	Co-BR	Ni-BR	Nd-BR
Tack	#3	#2	#1
Tear	#1	#2	#1
Compression set	#2	#3	#1
Rebound	#2	#3	#1
Abrasion	#3	#2	#1
Hysteresis	#2	#3	#1

Property , SBR/BR/N339	Co-BR	Ni-BR	Nd-BR
Tack	#2	#3	#1
Compression set	#1	#2	#1
Tear	#3	#2	#1
De Mattia bending	#2	#1	#1
Rebound	#2	#2	#1
Abrasion	#2	#2	#1

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re-elaborated compound data about Ni-BR and Nd-BR, which we retrieved from the literature.[2] Two Nd-BR pilot plant products having different branching levels are compared with Ni-BR. The results of data elaboration are shown in **Fig. 7**. The plot clearly shows that the lower the branching content the better results are found for rebound (higher), abrasion resistance (lower amount of abraded material) and heat build-up (lower hysteresis). On the contrary, when approaching structures with higher branching, the uncured compounds achieve lower Mooney viscosity.

High-cis Nd-BR with optimized structure

As discussed above, due to limited processability of Nd-BR during the transformation process typical of rubber compounding, polymer producers have lately undergone several industrial practices to increase the branching level of Nd-BR. So several structures are industrially possible for Nd-BR, which nowadays can range from mainly linear to highly branched architectures (**Fig. 6**). While high levels of branching can be achieved by applying post-modification processes, that is not the case of the optimized structures, which are the new Nd-BR grades proposed and commercialized by Versalis.

In particular, a high degree of branching is not beneficial to hysteretic properties, as already reported for SSBR.[6] Optimal compound properties are, then, a compromise between processing and end properties, since these two issues set conflicting requirements for the rubber. Slower extrusion speeds, lower processing temperatures and addition of processing aids are typically required to improve processability of Nd-BR, but these measures cause higher costs.

This conflict between superior properties of Nd-BR and challenging processing may be overcome by using specially designed grades. A summary of various performance aspects as a function of molecular design of Nd-BR is briefly reported in **Table 5**. Besides typical compound properties, it is important to remember that highly branched materials show reduced shelf life in terms of Mooney stability of the raw polymer during storage (Mooney rise phenomena), due to internal molecular rearrangements.[7]

The new Versalis Nd-BR grades featuring optimized structure can be the best solution for customers requiring enhanced properties of uncured compounds on top of excellent properties of the vulcanized rubber.

We introduce linear viscoelastic measurements to give an insight into the structures of the different Nd-BR under investigation. In **Fig. 8,** frequency sweep data of the raw polymers are arranged to represent a reduced Van Gurp-Palmen plot. This plot representation is widely adopted in the literature[8,9] as a valuable way to identify differences in terms of molecular architecture between different polymers. This way of plotting dynamic-mechanical data provides the advantage of being independent of test temperature, relaxation time, chemical composition and average molecular weight. In the reported picture, the phase angle, calculated from the loss tangent value at each measuring frequency, is represented as a function of a normalized rheological parameter, namely the ratio of the complex modulus $|G^*|$ and the rubbery plateau modulus G^0_N.

The phase angle is lower for materials with enhanced elastic properties and, for materials with similar polydispersity index, the Van Gurp-Palmen plot can account for the contribution of the branched patterns to the elastic response of the material. In **Fig. 8** we observe that Neocis BR45EP has a dynamic response, which lays in between the assumed reference structures, that is the linear and the highly branched Nd-BR materials (which are both model polymers). More precisely, with respect to the highly branched Nd-BR, Neocis BR45EP has much higher values of the phase angle, suggesting that the molecular structure of Neocis BR45EP is significantly different, with the material showing lower elasticity in the explored frequency spectrum. This difference of the phase angle value can be related with the different elasticity.[14]

Due to the known exponential dependence of rheological properties on branch length, the latter needs to be carefully designed to get the desired balance between processing and mechanical properties. It should be remembered, in fact, that processability can even become very bad if branching content and chain length both increase up to exceedingly high values.[15] Instead, when comparing the Neocis BR45EP curve with the one of reference linear Nd-BR, there is just an intermediate region of the Van Gurp-Palmen plot, where BR45EP shows a higher elastic response.

In **Fig. 9**, we show the different extrusion behavior of uncured tire compound for high abrasion resistance, which is rich in BR content (75 percent). To assess the advantages of Neocis BR45EP over a standard commercial BR type, we assume Neocis BR40 as reference material and we run a comparative extrudability test with Neocis BR45EP by means of a laboratory extruder equipped with a Garvey die. Although the pictures in **Fig. 9** do not represent the extrudates in the same scale, it is relevant to note the difference in the surface quality (flat surface and sharp corners) that the extrudates of the two different compounds achieve.

The extrudability of the uncured compound is positively impacted by the replacement of Neocis BR40 with Neocis BR45EP, while mechanical properties of BR45EP are comparable to those of BR40. Moreover, to better point out the optimum compromise between processability and hysteretic properties, Neocis BR45EP was tested in an SSBR/BR silica tread compound, where BR is the minor polymeric component. The Rolling Resistance Index is improved by 10 percent vs. the compound containing Neocis BR40.

To further prove the beneficial effect of the optimized structure, we finally consider Neocis BR61EP in comparison with Versalis Nd-BR standard grades, Neocis BR60 and Neocis BR40. All those materials were tested in sidewall NR/BR compounds and the results of Garvey extrusion are shown in **Fig. 10**.

The compound extrudate based on Neocis BR61EP is found to clearly show enhanced quality surface than the compound based on Neocis BR60. Furthermore, despite the Mooney viscosity difference between Neocis BR61EP and Neocis BR40, the optimized structure of Neocis BR61EP allows achieving competitive, and in this specific case, even superior Garvey results.

Fig. 7: Plot of cured compound properties as a function of the normalized compound Mooney for different high-cis BR types (nickel vs. neodymium BR). Polymers have different molecular architectures (branched patterns). We used different colors for each material type. Symbols having larger sizes account for increasing branching content of the raw polymer; the branching content is proportional to the ratio: (Mooney/Solution Viscosity). The values in the x-axis are calculated as: Compound Mooney/Reference Compound Mooney. Rebound, abrasion resistance and HBU (y-axis) were indexed with respect to the reference compound, so that higher values mean better performance. We assumed the Ni-BR-based compound as reference. Dashed lines are sketched for each compound property to improve data readability. We elaborated data taken from the literature.[2]

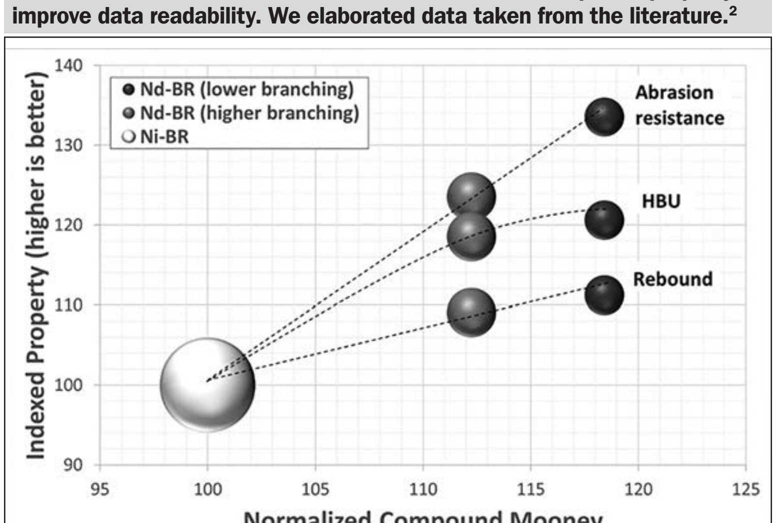


Table 5: Performance overview of different high-cis Nd-BR with different molecular architecture. The traditional reference BR has a mainly linear structure.

	Traditional Nd-BR	High Branching	Optimized structure
Raw polymer ageing	=	-	=
Compound viscosity	=	++	=
Compound extrudability	=	+	++
Compound hysteresis/abrasion	=	-	+

Fig. 8: Reduced Van Gurp-Palmen plot of the specially designed Neocis BR45EP vs. Nd-BR linear reference and Nd-BR highly branched reference. The reference samples (Nd-BR linear and Nd-BR highly branched) are model polymers.

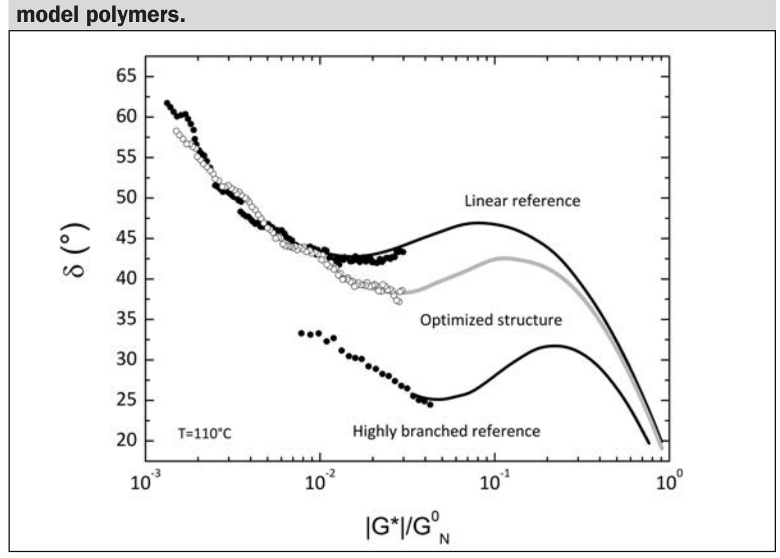
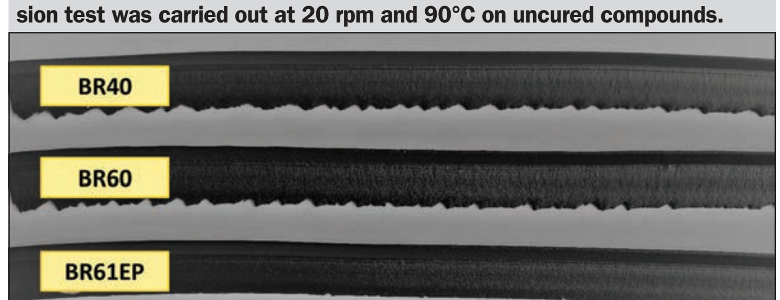


Fig. 9: Samples of uncured compounds extruded through the Garvey die of a laboratory extruder. The adopted compound formulation is for tire chafer. Polymers involved are BR/NR in ratio 75/25; filler type is N234 in amount of 75 phr. The Garvey extrusion test was carried out at 100 rpm and 90°C on uncured compounds after five days aging at room temperature. In the picture, the extrudates of the compounds with Neocis BR40 (above) and Neocis BR45EP (below) are compared.

Fig. 10: Samples of uncured compounds extruded through the Garvey die of a laboratory extruder. The adopted compound formulation is for tire sidewall. Polymers involved are BR/NR in ratio 50/50; filler type is N375 in amount of 45 phr. Mooney 60 polymers (Neocis BR60 and Neocis BR61EP) are compared with Mooney 40 material (Neocis BR40). The Garvey extrusion test was carried out at 20 rpm and 90°C on uncured compounds.



Acknowledgments

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