ALPHATECHNOLOGIES
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Gel Detection in Polymers by FT-Rheology via LAOS Technique

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Abstract. It is well known that not only the presence of long chain branching (LCB) but also the **gel content** in a polymer has a large impact on its viscoelastic properties and can affect significantly the processability of filled rubber compound (mixing process, black incorporation time, die swell, extrusion behaviour). The most direct way to determine gel content is via analytical techniques, by filtration of the polymer solution, however the absolute value of gel content in different commercial elastomer grades (e-SBR, e-NBR, NR) is difficult to assess and dependent on the applied method. There are some traditional rheological test methods that can be used to detect qualitatively the presence of macro-gel in raw materials. One of the most common ways in rheology to detect the gel is to check the stability of raw rubber. By performing a long-time sweep test the trend of the storage modulus vs. time provides an indication of the stability of the polymer. Additionally, the frequency sweep experiment can be used to provide an indication of the gel content. For elastomer produced by emulsion polymerization, very low tanδ values in the range of low frequency values could indicate that the material has a significant gel content.

In this study we propose an alternative approach, based on the advanced **FT-Rheology via LAOS technique**, that starting from the characterization of the non-linear response of raw materials, allows to quantify not only the LCB but also to **detect the gel content** in polymers. We have validated this approach by investigating several raw elastomers such as **Nd-BR**, **e-SBR**, and **NBR** grades and in this work, we show several case studies about this characterization.

1. Introduction

In addition to the main parameter of the molecular architecture, average molecular weight, molecular weight distribution (polydispersity), and degree of branching (short or long chain branching), **gel** is another very important element of the macrostructure of polymers that can have a considerable influence on processability of synthetic rubber and filled rubber compounds as well as on the property spectrum of the resultant vulcanizate. By definition, gel is not caused by branching or curing (curing agent) but is characterized by crosslink reaction between macromolecules. Gel fractions are characterized by extremely high Mw and/or crosslinked materials that cannot be dissolved in any solvent (highly branched insoluble molecule, also called macro-gel) and are removed by the filter.

As shown in figure 1 below, polymer gel-content is known either as inter-chain crosslinking (between two macromolecules) or as intra-chain crosslinking (between two side chains) mostly found in polymers with butadiene backbone (BR, e-SBR, and NBR).

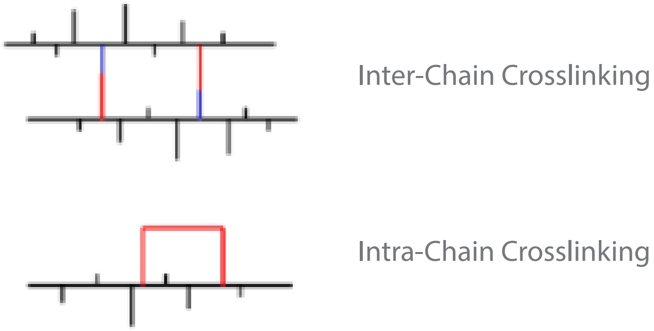


Figure 1: Definition of Gel

As already mentioned, the presence of gel in polymers has a large impact on processing behavior of the compound, due to its influence on the mixing behavior as well as flow properties during the extrusion process (on die swell and surface appearance of extrudate). High and/or variable gel levels cause problems. Commercial grades of elastomer synthetized by emulsion polymerization, e-SBR, NBR, with well-defined gel content have been developed for some specific applications. For those grades the presence of macro-gel improves the processing behavior of their compounds. When a large amount of reinforcing filler must be compounded, the compound tends to become crumbly and breaks into pieces. In this case, dispersion of carbon black is not achieved, and the compound cannot be formed into a shape. The presence of (large amounts) of gel can overcome this problem. Additionally, when green strength is needed for the mixed compound, long chain branching and even to some extent, the presence of gel are appreciated.

When comparing open mill mixing to an internal mixer, where the behavior of rubber compound cannot directly be observed, it is important to know the characteristics of raw material before mixing. The amount of macro-gel to be included in raw rubber to prevent mixing problems depends on the conditions and formulation. How much macro-gel should be contained in raw rubber to avoid the mixing problem depends on the conditions and formulation.

The presence of LCB and gel generates more free ends in vulcanizates compared with linear macrostructure. Such free ends increase heat build-up on finished products under repeated stressing. Gel is unwelcome in most instances since it influences die swell and surface appearance after extrusion and can change mechanical properties of the final products.

In general, gel formation and high LCB introduce very long relaxation times. There is also a strain hardening tendency. Even when the amount of these structures is very small, a few percent or less, it is known to cause various processing problems. **Die swell and waviness of the extrudate surface** (extrusion process) are related to this phenomenon.

Silica tread compound for tire application is mainly based on “green” elastomer grades that are polymerized in solution (batch s-SBR with functional group and Nd-BR). In this case the synthetic rubber manufactures try to produce polymers (for this application) that do not contain gel and to keep gel content in these materials to a minimum level for a specified period of time. However, it is not possible to guarantee this minimum gel level during, or after exposure to high shear and high temperatures in the mixer and for a long period of storage time. Depending on the level and type of stabilizers used in polymerization, level and type of antioxidant in compounding, and temperature level in mixing, some polymer lots may produce variable amount of gel during identical mixing conditions. In particular, the choice of the appropriate stabilizer/antioxidant agent that protect polymers against oxidation and the mechanism of degradation, by controlling molecular weight changes and gel formation (that lead to a loss of physical, mechanical properties) is sometimes a challenge for some rubber product and especially in the development of new elastomer grades. This can result in large variations in processability between batches of compound, increasing scrap and rework.

2. Techniques used to determine the gel content in polymers

The most common way in the rubber industry to determine the gel content in the elastomer is by applying analytical techniques. ASTM D3616 describes an analytical method for determining gel, swelling index and dilute solution viscosity. This method was developed to determine the gel content in e-SBR and NBR grades using specific solvents: toluene and methyl ethyl ketone, respectively. For NR and other commercial elastomer materials similar test methods have been developed using several types of solvents and operating conditions.

The literature states that results provided by all analytical methods cannot deliver absolute value of gel content because they depend on the choice of solvent, the time allowed for solubilizing, and of course on the temperature set in the defined procedure. ([3], [6], [23]) Additionally, when gel is present, analytical techniques like GPC cannot be used to determine the correct molecular weight and polydispersity of polymers. Therefore, in this case the use of rheology by measuring the viscoelastic properties of these materials is a promising way to overcome these limitations and to characterize the gel.

The most common test methods used in rheology to detect qualitatively the presence of macro-gel in the raw materials are time sweep, frequency sweep and stress relaxation testing.

Time sweep test is often used for the characterization of raw elastomers to check their stability. By performing a long-time sweep testing the trend of the storage modulus vs. time provides an indication of the stability of the polymer: a sharp increase of G′ indicates that the rubber is not stable due to the degradation and gel formation in the material. This method could be used as rough indication of the presence of a significant amount of gel in the rubber, as shown in figure 2.

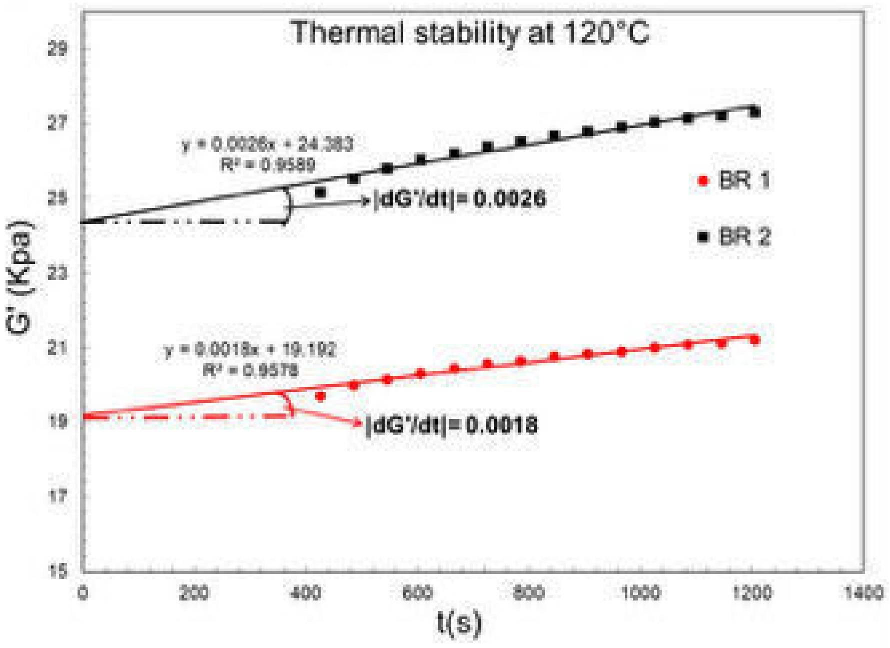


Figure 2: Time sweep test for checking the stability of raw elastomer

An oscillatory shear test performed in the LV region by **Frequency sweep** experiments is another standard approach that can be used to provide a qualitative indication of the gel content. It was observed that for elastomer grades produced by emulsion polymerization, the presence of a significant gel content can be detected by checking the tanδ vs. frequency plot: typically, very low tanδ values in the range of low frequencies allows to differentiate the different gel content in the examined rubber samples, see figure 3.

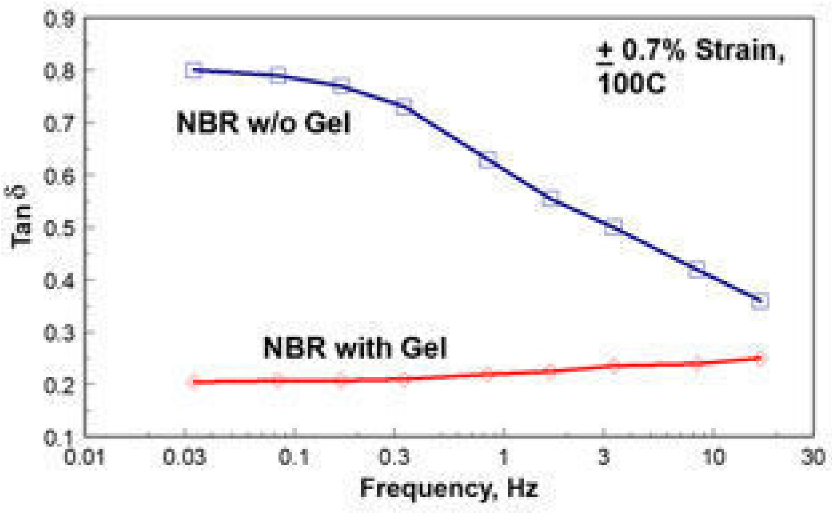


Figure 3: Frequency sweep test for comparing different gel content in the NBR samples

3. Introduction of FT Rheology via LAOS: LAOS technique to quantify long chain branching and gel content

Despite the influence of the molecular architecture of polymers on their viscoelastic properties is usually investigated by the linear viscoelastic characterization, this approach is not advanced enough to disclose information on complex branching patterns and for fully understanding the processing behavior of elastomers and thermoplastics materials.

In the non-linear region, the response of viscoelastic materials is no longer characterized by a sinus wave. The torque/stress signal is distorted: the higher the imposed deformation the more pronounced the distortion of the torque response, see figure 4.

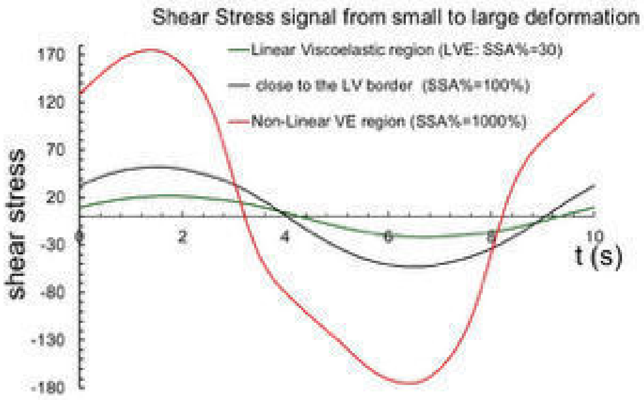


Figure 4: Distortion of the stress signal from small (linear region) to large deformation (non-linear regime)

The most common way to describe the real response of material tested in the nonlinear region (and quantify the distortion) is to apply FT-Rheology. That allows to account for all odd higher harmonics of the torque signal.

This approach was developed several years ago by A. Jeffrey Giacomin and John M. Dealy and is described in Techniques in *Rheological Measurement* ([14]). According to this theory the shear stress signal can be described as a Fourier series, which is as the sum of all odd higher harmonics of G' and G", see figure 5.

$$\tau = \gamma_0 \sum_{n=1}^{\infty} G'_n(\sin(n\,\omega t)) + G''_n(\cos(n\omega t))$$

$$G'_n(\omega) = \frac{\omega}{\pi}\int_0^{\frac{2\pi}{\omega}} \frac{\tau_0}{\gamma_0} \times sin(n\omega t)\,dt$$

$$G''_n(\omega) = \frac{\omega}{\pi}\int_0^{\frac{2\pi}{\omega}} \frac{\tau_0}{\gamma_0} \times cos(n\omega t)\,dt$$

Figure 5: Typical approach to describe the non-linear response by FT-Rheology

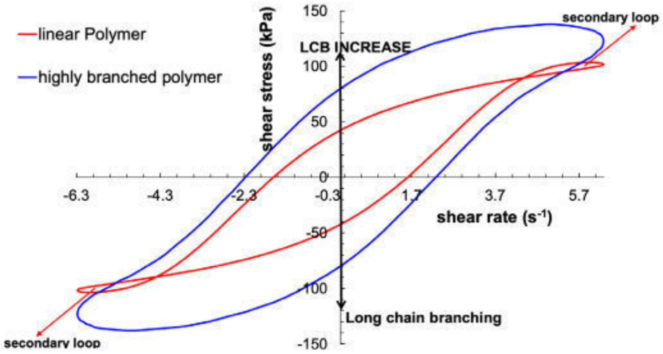


Figure 6: Lissajou figure comparison: linear polymer vs. branched polymer

LAOS responses can be visualized as parametric curves, called **Lissajous-Bowditch** figures of the oscillating shear stress, t(t) vs. strain γ(t), or t(t) vs. strain-rate, γ(t).

It was demonstrated that by the Lissajou figure, t(t) vs. γ(t), it is possible to distinguish between linear and branched polymers. In fact, secondary loops can only be attributed to polymers characterized by a completely linear macrostructure (could be due to polymer linearity irrespective of average molecular weight and molecular weight distribution). The increasing level of LCB separates the loading part of the stress signal from the unloading part thus, increasing the loop surface and balancing the distortion.

The mathematical criteria used to determine the analytical condition associated with the onset of the secondary loops was originally proposed by Stadler and Burhin et al. (2008) (Figure 7). Ewoldt and McKinley derived an alternative criterion based on the following condition: G'M < 0. G'M is the minimum-strain modulus used as a measure of non-linear viscoelasticity, and a negative G'M value indicates that the material is unloading elastic contributions to the instantaneous stress faster than new deformation is being accumulated.

To quantify the level of LCB in the polymers we defined a proper criterion, and we introduced two LCB indexes: **LCB 1** and **LCB 2**. The first one is the simple ratio between the first and the fifth harmonic component of G′ and following this criterion, the greater is this ratio the higher is the level of LCB in the polymer. The second LCB index comes from the theory that I have just shown you and it is mainly used to check the onset of these secondary loops. In fact, only polymers characterized by negative values of this LCB index show secondary loops.

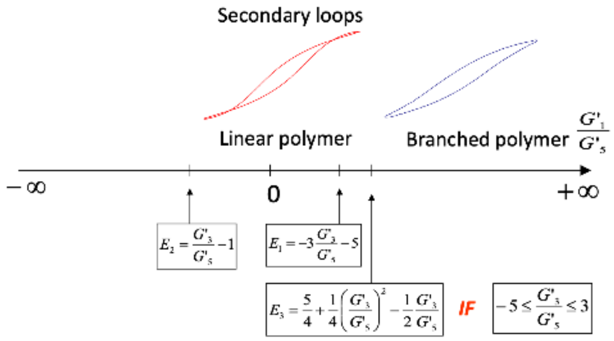


Figure 7: Lissajou figure comparison: linear polymer vs. branched polymer

- LCB index 1: $(G')_1/(G')_5$ → LCB 1

- LCB index 2: $(G')_1/(G')_5 - E_3$ → LCB 2

where E_3 is: $$\left[\frac{5}{4} + \frac{1}{4}\left(\frac{G'_3}{G'_5}\right)^2 - \frac{1}{2}\frac{G'_3}{G'_5}\right]$$

This approach is purely empirical but compared to other rheological test methods it has the advantage that it depends only on the degree of branching (LCB) and not on the other parameters of the macrostructure, polydispersity, MWD, and molecular weight, Mw, meaning both these indexes are insensitive to Mw and MWD.

As already mentioned, the generation of a macro-gel, highly branched insoluble fractions with extremely high molecular weight, begins with the formation of long branching. There is no clear knowledge about how many branches per molecule must form before it becomes insoluble. However, long chain branching and gel may be considered to be of the same kind but different in degree ([3], [24]).

Therefore, the above-mentioned LCB indexes can also be used to study the stability of raw elastomers, to detect the presence of gel and to quantity its content in polymers.

4. Approach used to quantify the gel content via LAOS

Aging effects, caused by long periods of storage of raw materials in the warehouse, and the use of unsuitable stabilizer in the polymerization, can result in a significant amount of gel in the polymer.
In this work we simulate the aging effects by heating the material at different temperatures for specific periods of time: typically, we put the samples into the oven at a certain temperature (70-100°C) for a few hours. Alternatively, the material can be aged in the RPA testing die by exposing the sample to high temperature and high shear for a few minutes.

By adopting the above second approach, the Premier RPA test procedure used to detect and quantify the gel content test procedures is based on the following three steps:

1. LAOS testing at 150°C on the sample before aging to determine the LCB indexes.
2. Aging or exposure of polymer to elevated temperatures and high shear.
3. LAOS testing at 150°C on the first sample after "aging" (after exposure to high temperatures and high shear) to determine the LCB indexes.

By comparing the Lissajou figures and LCB indexes it is possible to detect the presence of gel and quantify its content in the polymer (Figure 8).

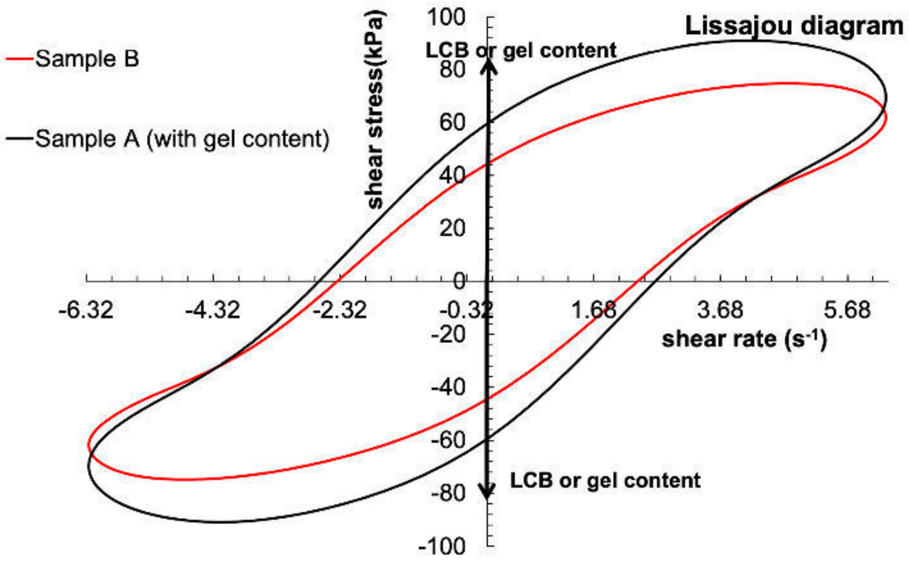


Figure 8: Lissajou figure comparison of samples with and without gel

5. Case Studies

To validate the approach presented in this work and also in the literature, we show several case studies in which we investigated several raw elastomer Nd-BR, e-SBR, NBR. Experiments were run on Alpha Technologies' Premier™ RPAs (RUBBER PROCESS ANALYZER) using the LAOS test method.

Case Study 1

In this study we checked the stability of a new BR experimental grade, BR 2 sample, and in particular the effectiveness of the stabilizer agent used to protect this polymer against oxidation, by controlling molecular weight changes and **gel formation**. We compared the viscoelastic properties of the new experimental material with those of a reference BR grade (stable material without gel), BR 1, using the above-mentioned techniques. These materials were synthetized by Ziegler–Natta polymerization leading to polybutadienes with a high cis-1,4 content (cis content between 91% and 98% is known as high-cis BR). Some characteristics of the molecular structure are summarised in the following table:

BR sample	Catalyst	cis-1,4	Mw	D	ML 1+4
		%	(g/mol)	(/)	(MU)
BR 1	Nd	98%	410000	2.1	43.0
BR 2	Nd	98%	430000	2.3	44.0

As already mentioned, we checked qualitatively the presence of macro-gel in the experimental BR grade by performing oscillatory shear tests in the LV region and comparing the trends of G′ vs. time (from time sweep testing) and tanδ vs. frequency (frequency sweep measurement) data obtained with the examined BR samples. By analyzing the results of the time sweep test at 110°C, it appears clearly that both samples show a similar trend (increase of G′ during the time) but the slope of the curve of BR 2, dG′/dt, is significantly higher than dG′/dt of BR 1. This indicates that probably BR 2 tends to oxidize quickly and produce gel, see figure 9.

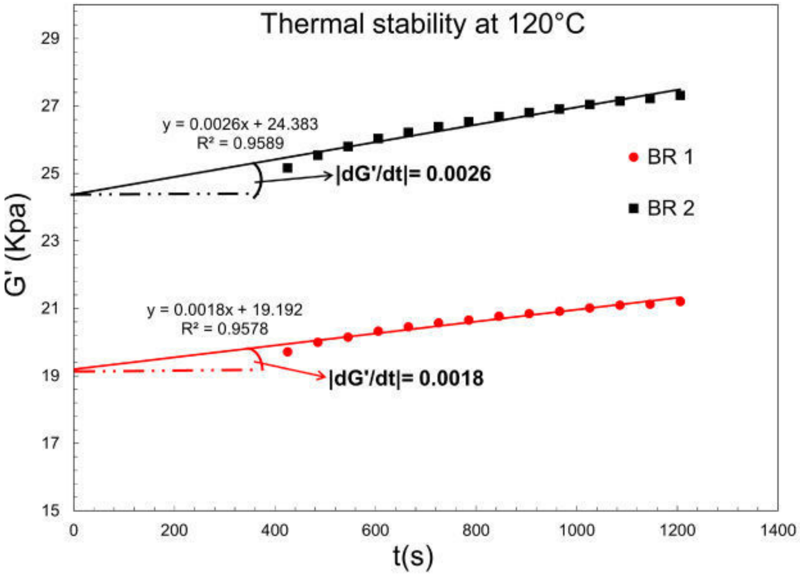


Figure 9: Time Sweep test comparison at 120°C

This was also confirmed by comparing tanδ of the investigated samples in the frequency sweep testing. In the range of very low frequency values tanδ of BR 2 sample is significantly lower than tanδ of sample BR 1 and this could indicate a large increase in gel content in this material during high temperature /shear condition, see figure 10.

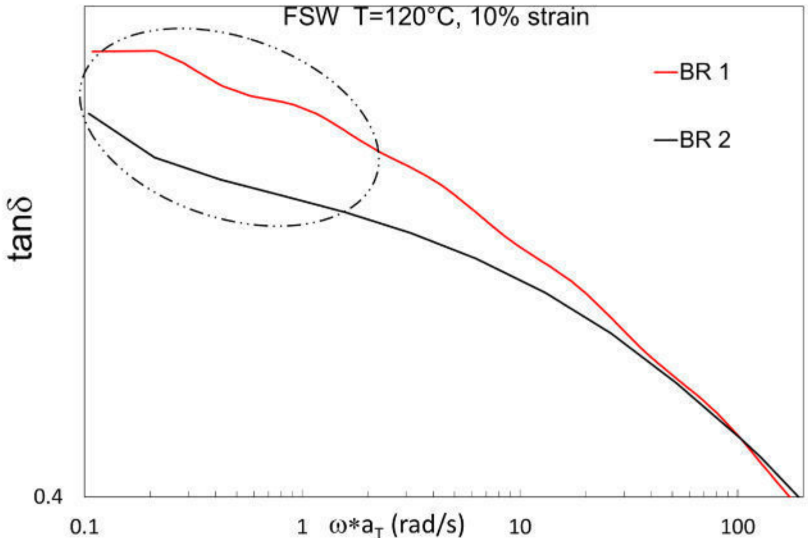


Figure 10: Frequency sweep test comparison to detect the gel content

To verify these results and to quantify the gel content in the experimental BR grade, we apply the FT-Rheology via LAOS technique. Additionally, to simulate the aging effects and the gel formation in the investigated material, we heated the material at the oven at 70°C for four days. We performed the LAOS experiment on the above-mentioned samples before and after heating.

By comparing the Lissajou figures of BR 2 sample before and after aging, it is possible to detect the significant increase of the loop area, shear stress vs. shear rate of this material due to the higher gel content in the annealed sample (Figure 11).

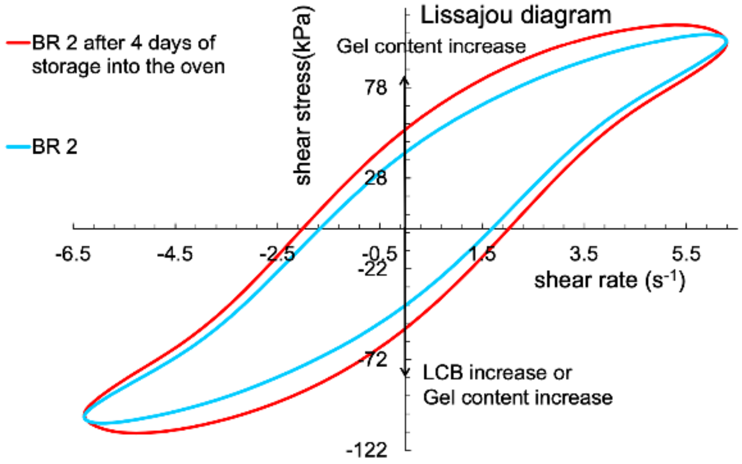


Figure 11: Increasing of the gel content of BR 2 sample during the time

The same comparison was also performed on BR 1 sample that did not show any difference before and after aging, see below.

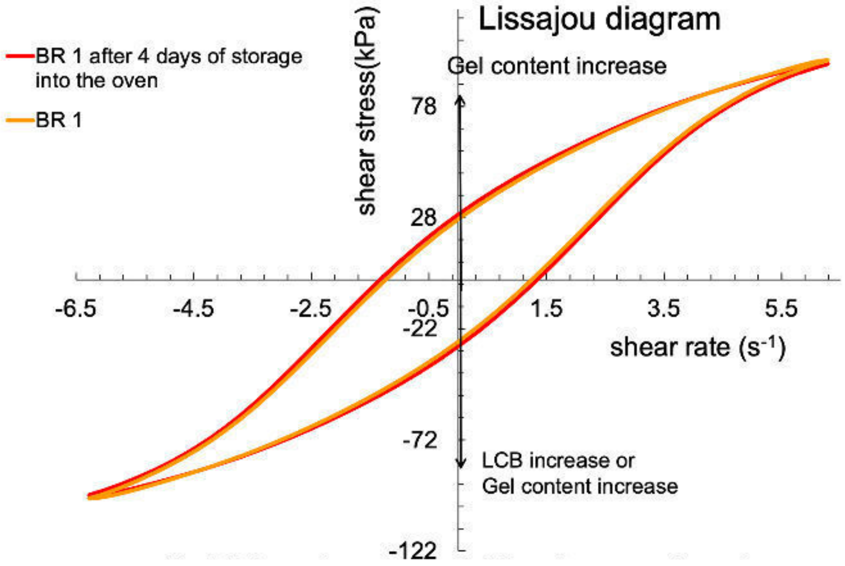
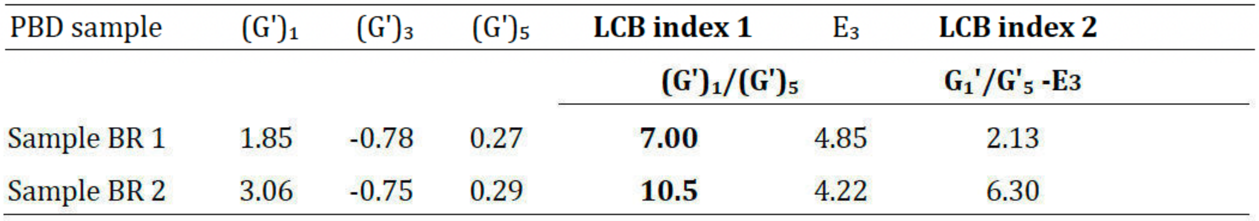


Figure 12: No change of BR 1 sample during the time

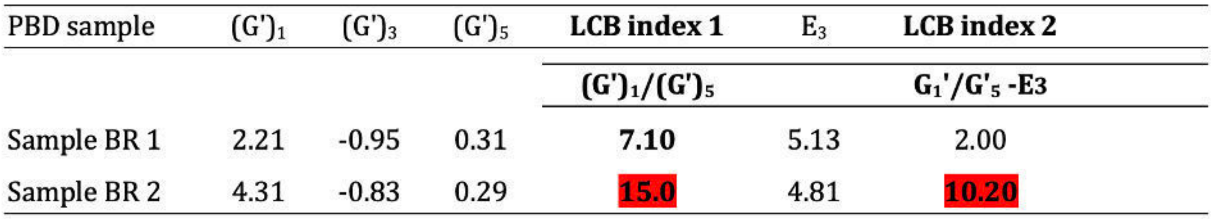
Using the above mentioned LCB indexes it is possible to quantify gel content in the examined samples confirming the high sensitivity of this test method:

Table 1. LCB indexes comparison of the investigated BR samples before aging PBD



PBD sample	$(G')_1$	$(G')_3$	$(G')_5$	**LCB index 1**	E_3	**LCB index 2**
				$(G')_1/(G')_5$		**G_1'/G'_5 -E3**
Sample BR 1	1.85	-0.78	0.27	**7.00**	4.85	2.13
Sample BR 2	3.06	-0.75	0.29	**10.5**	4.22	6.30

Table 2. LCB indexes comparison of the investigated BR samples after aging

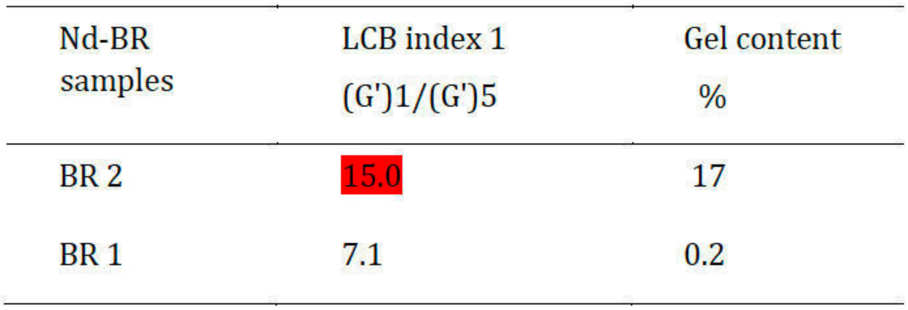


PBD sample	$(G')_1$	$(G')_3$	$(G')_5$	**LCB index 1**	E_3	**LCB index 2**
				$(G')_1/(G')_5$		**G_1'/G'_5 -E3**
Sample BR 1	2.21	-0.95	0.31	**7.10**	5.13	2.00
Sample BR 2	4.31	-0.83	0.29	**15.0**	4.81	**10.20**

The increase of the LCB indexes ratio during the time, confirms that the BR 2 sample is instable and have a significant gel content.

Using the above mentioned LCB indexes it is possible to quantify gel content in the examined samples confirming the high sensitivity of this test method:

Table 3. Correlation between the LCB index and the gel content



Nd-BR samples	LCB index 1 (G')1/(G')5	Gel content %
BR 2	15.0	17
BR 1	7.1	0.2

Finally, we have found an excellent correlation between the LCB index ($(G')_1/(G')_5$) obtained by the LAOS test, and the gel content measured by dissolving the rubber sample in toluene for 48 hours at room temperature without agitation.

Case Study 2

In this study we investigated the effects of gel in e-SBR on the compound processability in terms of extrusion behavior and filler dispersion. In this work we used the same 1502 e-SBR grade but produced from two different synthetic rubber manufacturers. As already mentioned, e-SBR 1502 is characterized by a broad molecular weight distribution, a high degree of LCB and additionally macro-gel. The molecular architecture of the investigated commercial grade is summarized in the following table:

e-SBR 1502 grade	PD	Mn	Sty	Vinyl	ML 1+4	branching
		(g/mole)	%	%	(MU)	
Samples: A, B	>4	115000	23.5	20	52	highly LCB

By comparing the investigated samples in the range of very low frequency values it appears clearly that tanδ of sample A is significantly lower than tanδ of sample B and this could indicate that materials have a different degree of LCB and probably a different gel content (Figure 13).

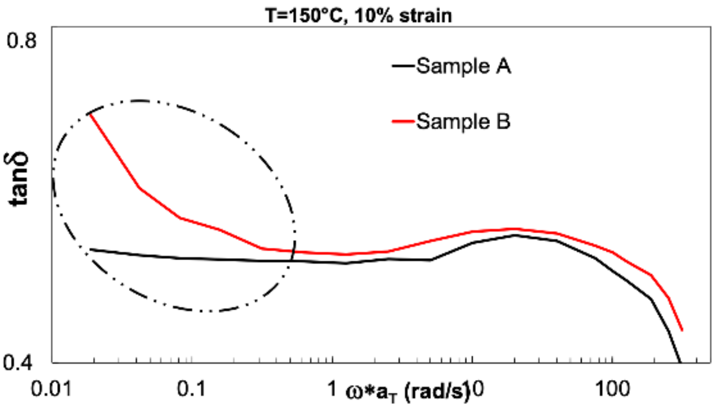


Figure 13: Comparison of loss tangent, tan(δ) at 110°C – sample A vs. sample B

By performing LAOS testing and comparing the Lissajou figure it was confirmed that the two examined samples are characterized by a different branching and probably gel content (Figure 14).

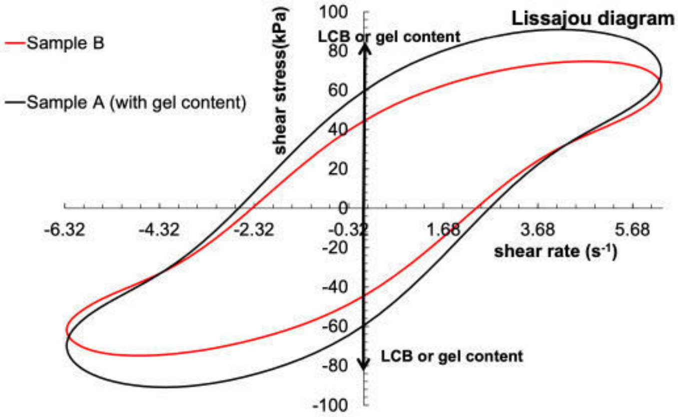


Figure 14: Lissajou figure comparison between sample A and sample B of same 1502 e-SBR grade

The presence of macro-gel in the sample A was detected by using the LCB indexes: the significant high value determined for sample A cannot only be due to the high branching content but also due to the presence of macro-gel in this material, see the comparison below:

e-SBR 1502	$(G')_1$	$(G')_3$	$(G')_5$	**LCB index 1** **$(G')_1/(G')_5$**	E_3	**LCB index 2** **G_1'/G'_5 -E3**
Sample A	4.35	-0.56	0.25	17.40	3.62	13.776
Sample B	3.90	-0.6	0.29	13.68	3.41	10.274

To study the extrusion behavior and the extrudability of the filled compound of the above mentioned samples, we performed extrusion measurements with a high-pressure capillary rheometer with slit die. In the slit die experiments the shear rate (the piston is controlled by motion of a driving piston) was imposed and the pressure gradient profile was measured by different pressure transducers mounted on the wide flat sides of the slit geometry. During the test the shear rate was changed step by step from 500 s-1 to 0.01 s-1.

As expected, the compound A containing macro-gel shows in the flow curve a significant higher shear viscosity than the compound B, and at the same value of extrusion rate a higher-pressure loss in the slit die, see figure 15.

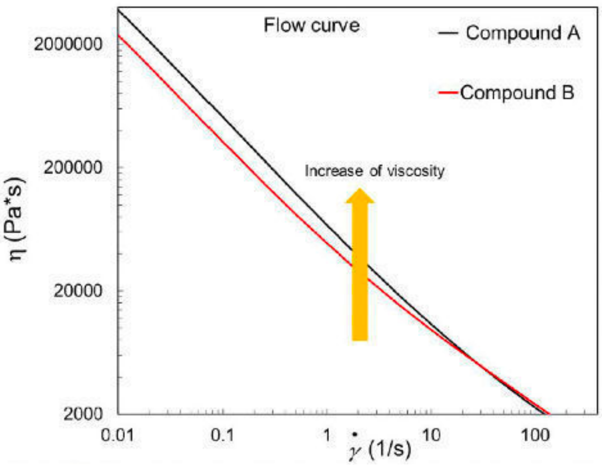


Figure 15: Comparison of flow curves between compound A and compound B

By the way, compound A shows a better extrudability in terms of surface quality of extrudate than compound B especially at high shear rate values which can be seen in figure 16.

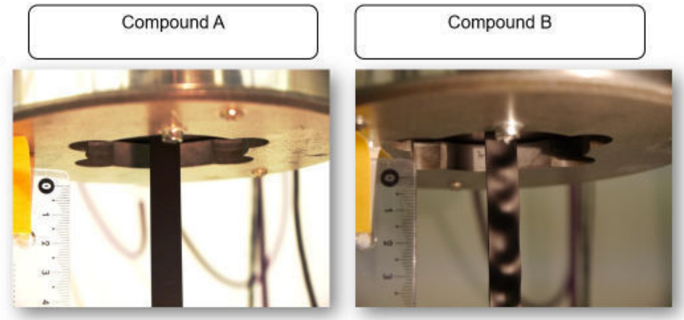


Figure 16: Comparison of extrudability between Compound A and Compound B at shear rate of 100 s-1

To evaluate the filler dispersion, we used the traditional Payne effect approach. The Payne effect is the measurement of dynamic strain softening of rubber compound in a strain sweep test: the difference of G' over the investigated range of strain is considered the Payne effect. Typically, the lower the ΔG' is the better the filler dispersion in the rubber matrix.

By comparing the ΔG' of the investigated compounds, using the traditional Payne approach, we should draw the conclusion that compound A should have a significant better filler dispersion than the compound B demonstrated in figure 17.

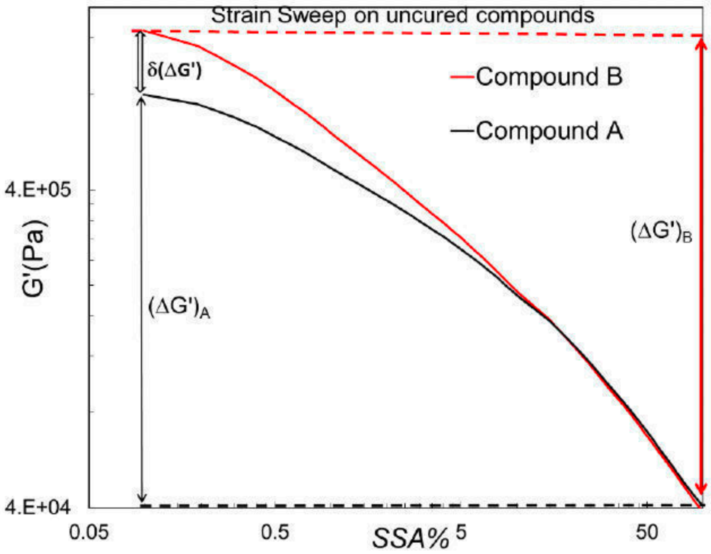


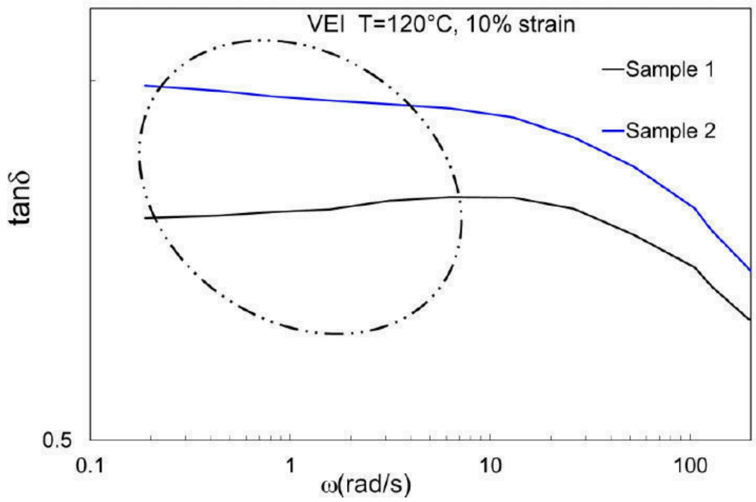
Figure 17: Payne effect comparison between Compound A and Compound B

Case Study 3

In this specific case we investigated two samples of the same NBR grade, produced by the same synthetic rubber manufacturer but received from two different lots. Despite the two examined materials have the same specification Mooney viscosity/Mooney Torque at standard conditions, i.e., ML(1+4) at 2 rpm and T = 100°C, the same acrylonitrile (ACN) content, (33%), it was observed a significant different behavior in the extrusion process, see the table below:

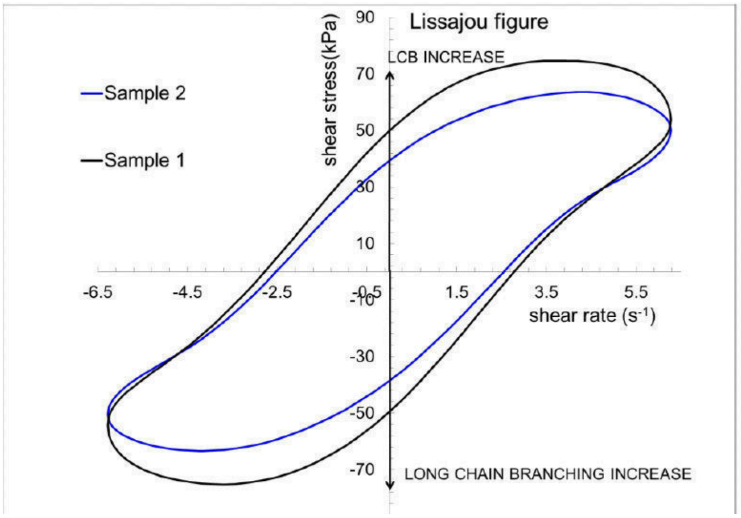
NBR grade	PD	Mn	ACN	ML 1+4	branching
		(g/mol)	%	(MU)	
Samples: 1, 2	>3	/	33	50	highly LCB

As already mentioned, NBR is synthetized by emulsion polymerization with a free radical initiator. Therefore, the mechanism of polymerization and branch/gel formation are very similar to the mechanism described for e-SBR.



Just by performing oscillatory shear test by frequency sweep experiments it was observed that two NBR samples have a completely different degree of LCB and probably a different gel content (Figure 18).

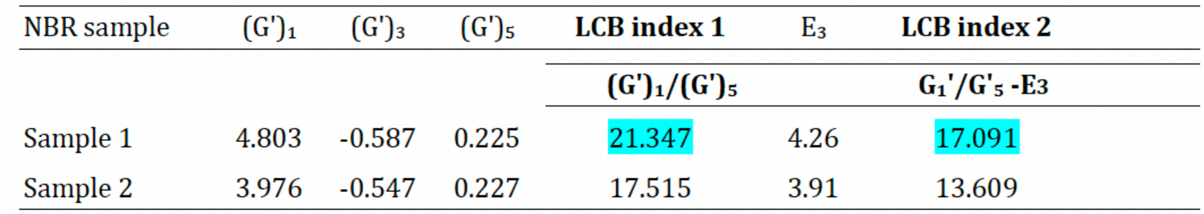
Figure 18: Frequency sweep testing for comparing the different NBR samples



By comparing the Lissajou figures of the investigated materials, it was possible to detect the different branching content and probably the significant gel content in sample 1, see figure 19.

Figure 19: Lissajou figure comparison between the same grade coming from two different lots

The presence of macro-gel in the sample 1 was confirmed by using the LCB indexes: the significant high value determined for sample 1 cannot only be due to high branching content but also due to the presence of macro-gel in this material, see the comparison below.



NBR sample	$(G')_1$	$(G')_3$	$(G')_5$	**LCB index 1**	E_3	**LCB index 2**
				$(G')_1/(G')_5$		**G_1'/G'_5 -E_3**
Sample 1	4.803	-0.587	0.225	21.347	4.26	17.091
Sample 2	3.976	-0.547	0.227	17.515	3.91	13.609

Table of LCB indexes comparison of the investigated NBR samples

The different gel content in the two examined materials determines a different flow behavior (Figure 20).

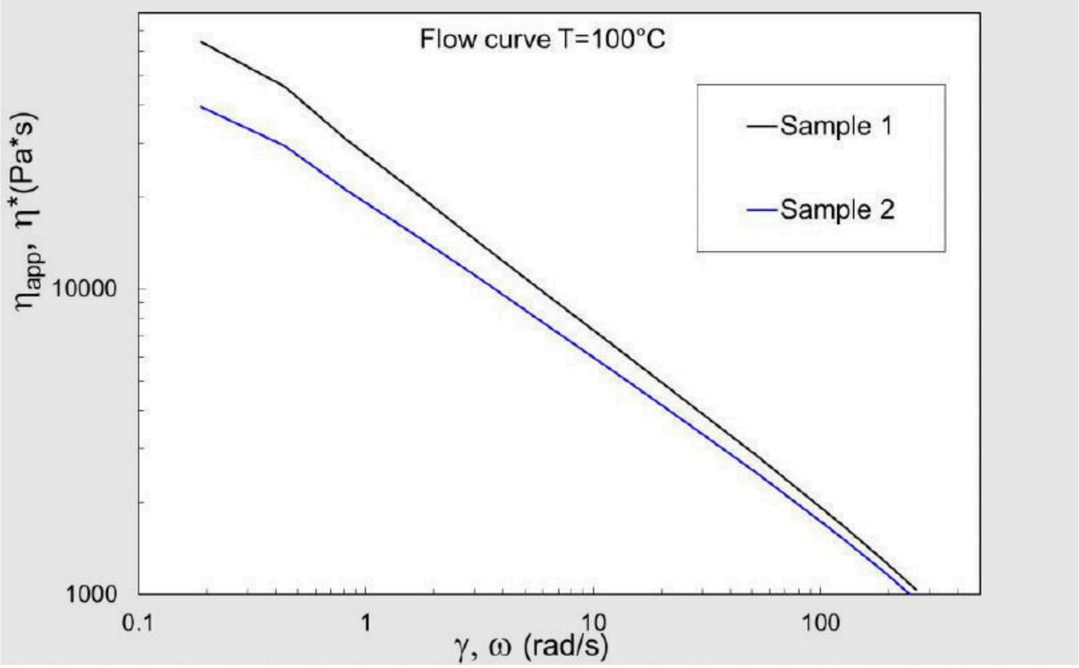


Figure 20: Comparison of flow curves between sample 1 and sample 2

The comparison of flow curve was obtained by carrying out frequency sweep tests at 100°C on the Premier RPA, assumed that the dynamic complex viscosity is equivalent to the steady shear viscosity, while frequency is equivalent to the shear rate, according to the Cox-Merz rule.

REFERENCES

[1] J. L. Leblanc, A. Mongruel, "A thorough examination of a torsional dynamic rheometer with a closed oscillating cavity," Rubber Plast. Technol., vol. 17, p. 162, 2001.

[2] J. S. Dick, H. Pawlowski, "Applications of the rubber process analyzer in characterizing the effects of silica on uncured and cured compound properties," presented at ACS Rubber Div. Mtg., Montreal, Canada, 1986, Paper 34.

[3] N. Nakajima, The Science and Practice of Rubber Mixing, Rapra Technology Limited, The University of Akron, USA, 2000.

[4] ASTM D3616, "Standard Test Method for Rubber, Raw-Determination of Gel, Swelling Index and Dilute Solution Viscosity."

[5] H. H. Winter, F. Chambon, "Journal of Rheology," vol. 30, p. 367, 1986.

[6] J. L. Leblanc, "Characterizing Gum Natural Rubber Samples Through Advanced Techniques," Journal of Applied Polymer Science, vol. 119, pp. 3058–3071, 2011.

[7] D. Ahirwal, M. Wilhelm, S. Filipe, "Journal of Rheology," vol. 58, p. 635, 2014.

[8] K. Hyun, M. Wilhelm, R. Ewoldt, G. H. McKinley, "Progress in Polymer Science," vol. 36, pp. 1697–1753, 2011.

[9] J. L. Leblanc, C. Chapelle, "Rubber Chemistry and Technology," vol. 76, p. 287, 2003.

[10] J. L. Leblanc, G. Nijman, "Journal of Applied Polymer Science," vol. 112, p. 1128, 2009.

[11] J. L. Leblanc, "Rubber Chemistry and Technology," vol. 86, pp. 261–285, 2013.

[12] H. Pawlowski, H. Burhin, C. Bailly, R. Keunings, "A study of polymer architecture with FT-rheology and large amplitude oscillatory shear (LAOS)," presented at IRC 2008, Monterey, California, 2008.

[13] W. Emunds, "Selection and QC of Raw Polymers by Evaluation of Gel Formation during Mixing," RPA 2000 Application Note, Alpha Technologies.

[14] J. Dealy, K. Wissbrun, Melt Rheology and Its Role in Plastics Processing, Chapman and Hall, 1995.

[15] C. W. Macosko, Rheology: Principles, Measurements and Applications, VCH Publishers, 1994.

[16] J. D. Ferry, Viscoelastic Properties of Polymers, John Wiley & Sons, Inc., New York, 1980.

[17] N. Nakajima, "Viscoelastic Characterization of Long Branching and Gel in Butadiene-Acrylonitrile Copolymer Elastomers," Rubber Chemistry and Technology, vol. 53, pp. 14–26, 1980.

[18] N. Tokita, I. Pliskin, "The Dependence of Processability on Molecular Weight Distribution of Elastomers," Rubber Chemistry and Technology, vol. 46, pp. 1166–1187, 1973.

[19] D. S. Campbell, K. N. G. Fuller, "Factors Influencing the Mechanical Behavior of Raw Unfilled Natural Rubber," Rubber Chemistry and Technology, vol. 57, pp. 104–117, 1984.

[20] W. Cousins, J. Dick, "Effective processability measurements of Acrylonitrile Butadiene Rubber using Rubber Process Analyzer tests and Mooney Stress Relaxation," presented at Rubber Division, ACS, Cleveland, Ohio, 1997.

[21] S. Kawahara, Y. Isono, "Effect of Gel on the Green Strength of Natural Rubber," Rubber Chemistry and Technology, vol. 75, pp. 739–746, 2002.

[22] N. Nakajima, E. R. Harrell, "Viscoelastic Characterization of Long Branching and Gel in Elastomers by Comparison of Large and Small Deformational Behavior," Rubber Chemistry and Technology, vol. 60, pp. 742–760, 1987.

[23] J. Puskas, C. Hefler, "Natural Rubber Biosynthesis: Still a Mystery," Rubber Chemistry and Technology, vol. 91, pp. 683–700, 2018.

[24] F. Bacchelli, "Rheological Implications of the Reduction in Viscosity of SBR Copolymers During Mixing," KGK, vol. 04, pp. 188–191, 2008.