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Decoding Nonlinear Viscoelasticity: Generalized Moduli from Strain-Controlled Shear Analysis

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Abstract

This study explores the transition from linear to non-linear viscoelastic behaviour in polymers subjected to cyclic sinusoidal shear deformation. The stress response is analysed using Fourier series decomposition, enabling the characterization of the generalized elastic modulus, $G_0^{'}(\gamma_0)$ and the viscous modulus. These parameters are essential for describing the complex viscoelastic properties of polymers. It is demonstrated that $G_0^{'}(\gamma_0)$ consists of two distinct contributions: the first harmonic, representing the linear elastic response, and the non-linear modulus, $G_{NL}^{'}$, which arises from all higher harmonic components. Additionally, the study introduces a well-defined nonlinearity index, expressed as the ratio of $G_{NL}^{'}$ and $G^{'}$ to further analyse the viscoelastic behaviour under dynamic shear deformation.

Keywords: Nonlinear viscoelasticity; LAOS; Generalized Viscoelastic Moduli; Nonlinear Behavior; Nonlinearity Index (NLI)

Introduction

Measurement of viscoelastic properties in polymers, across a wide range of deformations, is commonly performed using a Rubber Process Analyzer (RPA). This strain-controlled rheometer is specifically designed to provide reliable viscoelastic data under varying strain, frequency, and temperature conditions in a simple, repeatable, and reproducible manner. The RPA operates by subjecting polymer samples, in their molten state, to cyclic sinusoidal shear deformation within a biconical, closed, and sealed die cavity. During testing, the lower die oscillates under controlled strain and frequency conditions, while the upper die remains stationary. The shear stress generated by the sample against the upper die is recorded by a torque transducer, which measures stress over time during each oscillation cycle.

To comprehensively analyse viscoelastic behaviour, the stress signal over time can be decomposed into its characteristic frequency spectrum using Fourier series analysis. This approach is particularly effective for studying uncured polymer compounds under deformation, as it provides a detailed representation of the stress response. In the linear viscoelastic regime, the relationship between strain and stress is proportional, allowing for the unambiguous determination of the elastic component, known as the storage modulus (G′), and the viscous component, known as the loss modulus (G′′). While the linear viscoelastic behaviour of polymers is well understood, significant research has also been conducted to characterize their nonlinear behaviour under large amplitude oscillatory shear (LAOS) deformation. [1] LAOS testing, often used to study filled rubber systems, has been extensively applied to analyse the nonlinear viscoelastic response of polymers. Previous studies [2–5] have primarily focused on quantifying the nonlinear response by examining the ratio of the third harmonic contribution to the first harmonic. Additionally, harmonic analysis has been applied to silica-filled rubbers, providing insights into the complex interactions between fillers and the polymer matrix [2].

This paper aims to advance the understanding of polymer behaviour under cyclic sinusoidal shear deformation, regardless of the applied strain level. By adopting a unified approach, this study ensures that the analysis remains applicable across a wide range of deformation conditions, capturing the full spectrum of viscoelastic responses. A detailed mathematical framework, based on the theory of generalized viscoelasticity [6], is presented to provide a rheological fingerprint for uncured polymer compounds. Beyond the theoretical analysis, this work demonstrates the practical application of the approach to various scenarios, including the viscoelastic behaviour of linear and branched polymers. These

analyses reveal differences in molecular architecture among commercial rubber grades and enable the quantitative evaluation of filler-rubber interactions in diverse compound formulations. By bridging the gap between theoretical models and real-world applications, this study contributes valuable insights to both academic research and industrial practice. The findings presented here aim to enhance the understanding of polymer viscoelasticity, offering a robust framework for characterizing complex materials and optimizing their performance in practical applications.

Generalized Viscoelastic Moduli

A sinusoidal deformation is applied to a polymeric material in a molten state according to Equation 1:

$$\gamma(t) = \gamma_0 \sin \omega t \quad (1)$$

where γ(t) refers to the shear deformation over time and γ_0 the maximum value of the deformation (strain) during the cycle at a frequency ω.

The torque output signal S(t) is analytically described using the trigonometric Fourier series of sine and cosine periodic functions, as follows:

$$S(t) = \sum_{k=1} S_k^{'} \sin(k\omega t) + S_k^{''} \cos(k\omega t) \quad (2)$$

The shape factor of biconical geometrical, $\frac{3}{2\pi R^3}$, where R is the radius of the cavity allowing to convert the torque S into the corresponding shear stress, τ [7]. Considering that strain is an odd function of time $\gamma(-t) = -\gamma(t)$ it follows it follows that the corresponding stress components are also odd functions of time. By decomposing the Fourier series representation of the stress, τ(t) into its odd and even components, it becomes evident that the sine terms, being odd functions, constitute the elastic stress component. The relationship is expressed as follows:

$$\tau_E(t) = G(\gamma(t)).\gamma(t) = \left(\frac{3}{2\pi R^3}\right) \cdot \sum_{k=1,3,5,..} \left[S_k^{''} \sin(k\omega t)\right] \quad (3)$$

Similarly, the cosine functions, which are even functions, represent the viscous stress component. It is important to note that the first harmonic of the elastic term is in phase with deformation, whereas the first harmonic of the viscous term is quadrature with the strain. This decomposition provides a clear analytical framework for distinguishing between the elastic and viscous contributions to the overall stress response in viscoelastic materials.

The generalized shear stress undergoing cyclic sinusoidal shear deformation can therefore be written as follows:

$$\tau(t) = \tau_E(t) + \tau_V(t) \quad (4)$$

In terms of strain γ (deformation) and shear rate γ˙ the generalized shear stress equation (4) can be written as:

$$\tau(\gamma, \dot{\gamma}) G(\gamma).\gamma + \frac{1}{\omega}.W(\dot{\gamma}).\dot{\gamma} \quad (5)$$

where $G(\gamma)$ represents the generalized elastic modulus, which depends solely on strain, while $W(\dot{\gamma})$ denotes the generalized viscous modulus, which depends solely on the shear rate [8]. It is important to emphasize that Equation 5 is independent of the type of viscoelastic regime, whether linear or particularly nonlinear. In the context of linear viscoelasticity, generalized moduli $G(\gamma)$ and $W(\dot{\gamma})$ simplify to G' and G" respectively.

$G(\gamma)$ versus γ, can be obtained using specific forms of angle identities or Chebyshev polynomial by using Eq.6 such as

$$G(\gamma(t)) = \frac{\tau_E(t)}{\gamma(t)} = \sum_{k=1,3,5...} \left[\frac{\tau_k^{'}}{\gamma_0} . \frac{\sin(k\omega t)}{\sin(\omega t)}\right] \quad (6)$$

where the G generalized elastic modulus depends on the cycle amplitude and varies with the strain γ. Expanding the Fourier series as shown by Equation 6, it is possible by rearranging the terms of the sum, and using the definition $\sin \omega t = \gamma / \gamma_0$ to get the following equation 7:

$$G(\gamma, \gamma_0) = \frac{\tau_1^{'}}{\gamma_0} + \sum_{n=1}^{\infty} (2n+1) \frac{\tau_{2n+1}^{'}}{\gamma_0} + \sum_{n=1}^{\infty} (-1)^n g_{2n+1} \left(\frac{\gamma}{\gamma_0}\right)^{2n} \quad (7)$$

In particular $\frac{\tau_1^{'}}{\gamma_0}$, is the well-known linear viscoelastic modulus, known as G' for a shear cycle strain deformation γ_0 at γ =0. All non-linear components $G_{2n+1}^{'} = \frac{\tau_{2n+1}^{'}}{\gamma_0}$ can be written as a linear combination of non-linear stress components such as:

$$G_{NL}^{'}(\gamma_0) = \sum_{n=1}^{\infty} (2n+1) \frac{\tau_{2n+1}^{'}}{\gamma_0}$$

In particular $G_0^{'}$, is defined as is generalized modulus obtained by a linear combination of a modulus purely generated by the first harmonic and a modulus resulting in all non-linear components $G_{NL}^{'}$ as follows:

$$G_0^{'} = G^{'}(\gamma_0) + G_{NL}^{'}(\gamma_0) \quad (8)$$

The last term accounts for elastic modulus change during cycle deformation $\gamma = \gamma_0 \sin \omega t$ where the parameters g_n can be calculated by equation 9 such as i.e.

$$g_3 = 4G_3^{'} + 20G_5^{'} + 56G_7^{'} + 120G_9^{'} + \ldots + mG_{2n+1}^{'}$$

Parameters of equation 7, can be easily calculated as follows for 9 harmonics Fourier series:

$$\begin{bmatrix} G_0^{'} \\ g3 \\ g5 \\ \ldots \\ gn \end{bmatrix} = [a_{i,j}] \begin{bmatrix} G^{'} \\ G_3^{'} \\ G_5^{'} \\ \ldots \\ G_n^{'} \end{bmatrix} \quad a_{i,j} = \begin{cases} 2^{2(i-1)_0^{2,j-1}} (j-i+1)! \\ \begin{bmatrix} if\ \ i=1\ (first\ row) \\ if\ \ i \geq 2 if\ \ j \geq i \\ if\ \ j < i \end{bmatrix} \end{cases} \quad (9)$$

with $i, j = 1, 2 \ldots \frac{n+1}{2}$

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The same approach can be used to calculate W(γ˙) as a power series of γ˙ and can be written as follows:

$$G_0^{''} = \frac{\tau_1^{''}}{\gamma_o} + \frac{-3\tau_3^{''} + 5\tau_5^{'} - 7\tau_7^{''} + 9\tau_9^{''} - \ldots + (2n+1)\tau_{2n+1}^{''}}{\gamma_o}$$

From Linear to Non-Linear Viscoelastic Behaviour

It is worth reminding that at low deformation cycle amplitude, that in rheological terms means linear viscoelastic regime and $\lim_{\gamma_o \to 0} G_{NL}^{'} = 0$.

Based on these results, it becomes apparent that when high-order harmonics of the applied deformation cycle appear in the shear stress, the nonlinear viscoelastic regime is in effect. It is crucial to emphasize that the modulus generated by the first harmonic $G^{'}(\gamma_0)$, is dependent on the cycle deformation γ_0 and its behaviour can only be determined experimentally. Conversely, in the presence of non-linear viscoelastic behaviour, the stress curves can be represented by a Fourier series consisting of odd harmonics of the deformation cycle.

Given these considerations, it is possible to introduce a useful index of non-linearity, denoted as $NLI = -G_{NL}^{'} / G^{'}$ which indicates the extent to which the non-linear term (including all non-linear components) contributes compared to the linear contribution (the modulus of the first harmonic) at a given deformation. In other words, this non-linear parameter provides a more precise description of the non-linear response of viscoelastic materials. This parameter is known as the ratio between the moduli of non-linear components only and the elastic modulus $G^{'}(\gamma_0)$ from the first harmonic only. As previously shown, NLI is equal zero in the linear regime.

For filled rubber materials, the challenge is to determine the strain values within which the material behaves as a linear viscoelastic solid [9]. Nonlinear viscoelastic behaviour is typical of filled rubber compounds and is associated with the loss of proportionality between stress and strain, or, in signal terms, with harmonic distortion. The Payne effect, observed in cured compounds, is characterized by a reduction in the elastic modulus as the strain amplitude increases. An in-depth understanding of the Payne and Mullins effects [10,11] is crucial for accurately interpreting the performance characteristics of filled rubber compounds. As the strain amplitude increases, the material exhibits pronounce non-linear behaviour, which complicates the analysis and interpretation of these phenomena. Therefore, careful consideration of the instrument's limits and the material's response is essential for accurate characterization.

Experimental

Polymers and compounds were tested using the RPA (Rubber Process Analyzer), manufactured by Alpha Technologies (a company of the Indicor Group, Hudson, OH, USA). The tests were conducted at a frequency of 0.5 Hz and a temperature of 150 °C, utilizing cyclic sinusoidal shear deformation. The RPA is equipped by a biconical testing die cavity with a closed rim and grooved dies, which help minimize slippage and enable the testing of very stiff materials.

Seven commercial polymers were investigated. Specifically, from Versalis: plastic materials tested includes Flexirene FG 20 LLDPE, a linear polyethylene, and Riblene FF 30 LDPE, a highly branched polymer. For rubber-like polymers, Europrene e-SBR 1500 (SBR), Europrene N 3330 (NBR), and the higher viscosity grade NBR Europrene N3360 were also tested. Additionally, s-SBR4602, a solution Styrene Butadiene Rubber (s-SBR) from Trinseo's SPRINTAN grade, and Cariflex IR0310, a high cis-1,4 polyisoprene from KRATON, were included in the study.

Rubber compounds were also part of this research. An internal laboratory mixer (Banbury mixer with a chamber of 1 liter volume) was used to compound NBR with two grades of carbon black (N115 and N550).

These model formulations are used to study the shear deformation behavior of the polymer-filler matrix and to shed light on the interactions that generate reinforcement, which are fundamental to the performance of the rubber compound.

The deformation γ_0, defined as the cycle amplitude deformation multiplied by 100 in the range of 0.1% to 800%) was applied through oscillatory shear conditions. The effect of strain deformation γ_0 on $G_0^{'}(\gamma_0)/G^{'}$ shows an S-shaped degrowth behavior as given in (Figure1) mainly independent of the polymer chain type. The linear viscoelastic regime is characterized by the typical "plateau" of the elastic modulus and between 10 to 30% it is possible to observe a general transition behavior to a nonlinear region. It is important to underline that $G_{NL}^{'}(\gamma_0)$ always assumes a negative value which implies that $G_0^{'} \le G^{'}$.

In the nonlinear viscoelastic region, it is noteworthy that the slope of the curve is approximately 0.8. This observation holds true irrespective of whether the polymer chains are linear or branched in the molten state. Such behavior underscores that the generalized elastic modulus adheres to a master curve, thereby demonstrating a consistent and predictable physical response across different polymer architectures. From both an analytical and rheological perspective, the normalized $G_0^{'}$ is not the most suitable parameter for providing a unique material identification (Figure 2).

The behavior of viscoelastic materials is described using a more sensitive non-linear parameter given by the ratio between sum of all moduli of nonlinear harmonic and G' as following

$$NLI = -G_{NL}^{'} / G^{'}$$

It is important to emphasize that s-SBR 4602 exhibits the behavior characteristic of a linear chain polymer. This contrasts with the result obtained for the well-known e-SBR 1500, a general-purpose emulsion styrene-butadiene rubber obtained through cold polymerization, which demonstrates the typical characteristics of a branched polymer chain (Figure 3).

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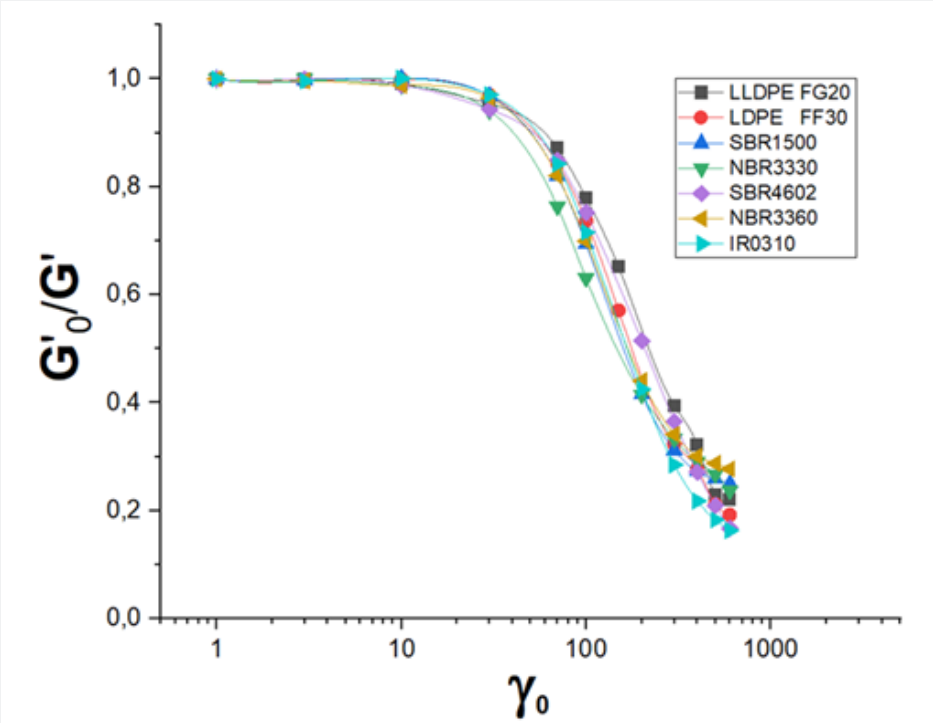

Figure 1: Transition between the linear and the nonlinear region by using Generalized elastic modulus normalized by G' at cycle strain equal to γ=0.

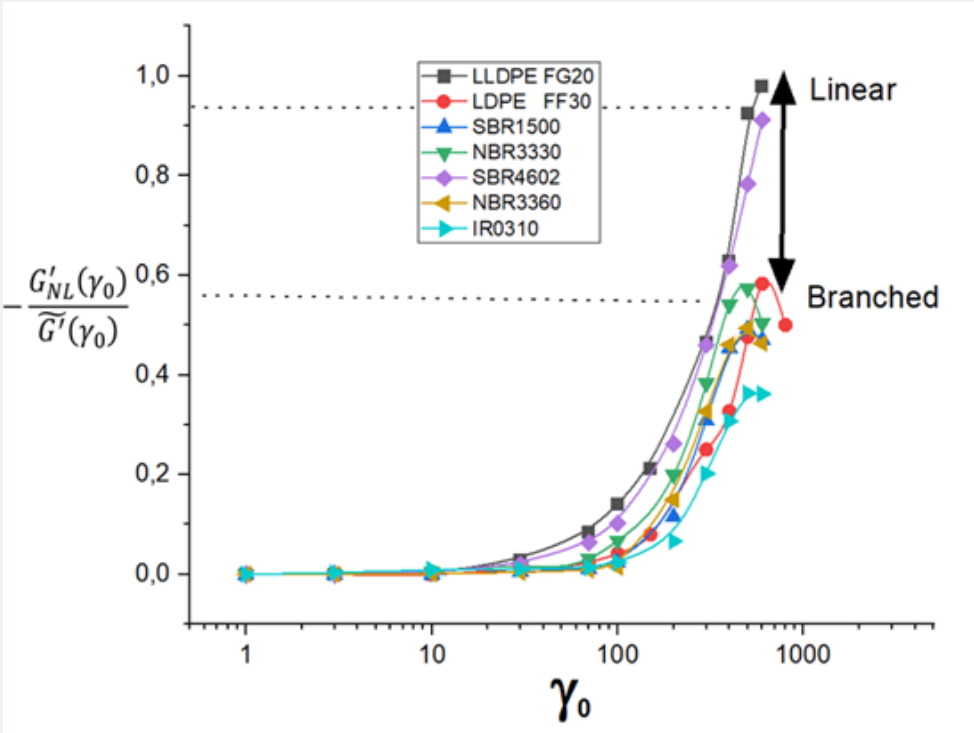

Figure 2: Non-Linear Index $NLI = -G'_{NL} / \tilde{G}'$ as a function of strain (deformation) for various polymer architectures.

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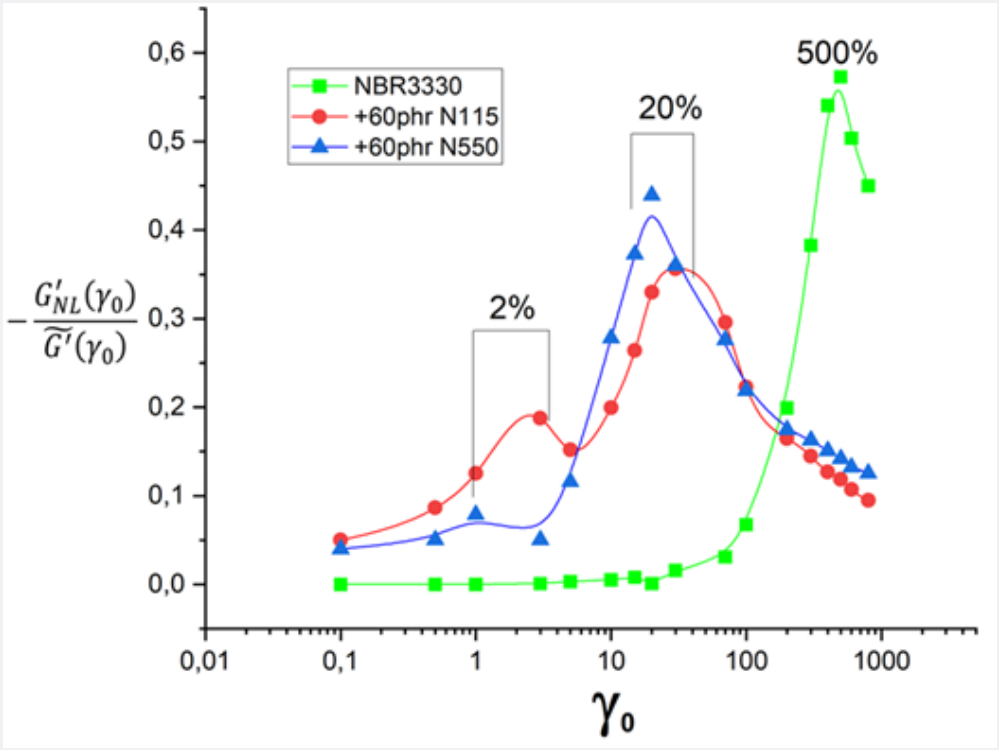

Figure 3: Rubber-filler interaction NBR compounds explored in a wide range of strain by using NLI.

In this study, we also examined compounds made from Nitrile Butadiene Rubber (NBR3330) with carbon black, specifically grades N115 and N550, at the same level of filler content (60%).

The graph clearly illustrates the reinforcing effect of the filler, which induces significant non-linearity. This observation can be utilized to classify the reinforcing effect of a given carbon black and the degree of induced non-linearity. The reinforcement of elastomers through the incorporation of fillers has been extensively investigated across numerous studies [12,13]. It is widely acknowledged that the effectiveness of this reinforcement is largely influenced by the properties of both the polymer and the filler, as well as the processing conditions.

The mechanisms governing the nonlinear viscoelasticity of filled elastomers were investigated using non-linear rheological investigations (NLI). Trapping elastomer chains at the filler surface leads to an increased entanglement density, which varies with distance from the filler surface. As illustrated in (Figure 3), the loss of trapped entanglements due to the strain-induced debonding of chain segments from filler surface, facilitates the relaxation of the matrix entanglement structure, resulting in the observed primary peak. In (Figure 3) it is also shown that for N115, the NLI response is significantly more pronounced than for N550, likely indicating a greater extent and strength of the adsorbed chains. Additionally, a second peak around 20% shear strain is observed, which is nearly independent of the filler structure used in the compound. This second peak can therefore be associated with polymer-filler interactions. It is crucial to emphasize that for branched polymers subjected to high strains (ranging from 400% to 600%), the ratio $-G'_{NL}/G'$ exhibits a pronounced maximum, followed by a sharp decrease as the strain amplitude γ_0 increases further higher.

Results and Discussion

This study presents an analytical characterization of the viscoelastic behavior of polymers, emphasizing both the fundamental insights and practical implications. Traditional theories of elasticity primarily address linear viscoelasticity; however, the intricate mechanical behavior of rubber under large deformations necessitates a more comprehensive examination of nonlinear aspects. Shear stress resulting from pure sinusoidal shear deformation has been analyzed using a Fourier series approach. The stress response at any deformation is resolved into its elastic and viscous contributions.

The concept of the generalized elastic moduli has been introduced, which accounts for the modulus component in phase with the deformation frequency, alongside other moduli derived from higher harmonics that emerge in the nonlinear regime. When the deformation amplitude,γ_0, increases, the first harmonic component of the modulus, $G'(\gamma_0)=\frac{\sigma_1}{\gamma_0}$,which is constant in the linear

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viscoelastic region, becomes amplitude-dependent and begins to decrease. Concurrently, additional stress components $\frac{\tau_3'}{\gamma_0}, \frac{\tau_5'}{\gamma_0}, \frac{\tau_7'}{\gamma_0}$... etc, combined into the generalized nonlinear modulus $G_{NL}'(\gamma_0)$ become increasingly significant. Consequently $G_{NL}'(\gamma_0)<0$ assumes negative values, as confirmed by the experimental data. To quantify the effect of these higher harmonic nonlinear components a Non-linearity Index (NLI) has been defined. The NLI serves as a clear criterion for distinguishing the transition from linear to non-linear viscoelastic behavior in rubber materials. Through comparative analysis of experimental results, it is evident that the NLI as a function of strain can differentiate between linear and branched polymers. Specifically, branched polymers exhibit a pronounced peak in NLI between 400% and 600% strain, followed by a sharp decrease. Due to the absence of a comprehensive chain dynamics model under strain, these observations provide only a qualitative understanding of the distinct behaviors. The study highlights significant non-linearity induced by these fillers, depending on the type. For instance, a notable peak at approximately 3% strain was observed for N115 at 60 phr, which is attributed to the intense absorption of rubber chains on the filler surface, as corroborated by existing theoretical models.

In conclusion, this work sheds light on the complex non-linear viscoelastic behavior of polymers and compounds, emphasizing the critical role of fillers in enhancing their properties. The findings underscore the potential of the NLI as a valuable tool for probing the intricate interactions within polymer matrices, paving the way for improved material design and application.

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