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Research Article

Unveiling Branching Structures in Synthetic Rubbers: Insights from Phase Angle Studies Using a Rubber Process Analyzer

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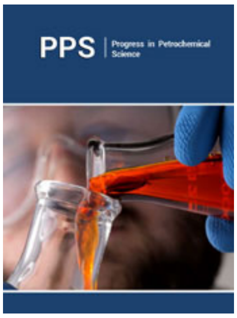

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Abstract

Understanding how branching affects the properties of synthetic rubbers like Butadiene Rubber (BR) and Styrene-Butadiene Rubber (SBR) is important for improving their performance in various applications. In this research, we used a Rubber Process Analyzer (RPA) to perform a phase angle vs. frequency test, which helps us to learn more about the rubber's behavior under different conditions. The RPA test measures how the rubber responds to different frequencies, giving us detailed information about its mechanical properties. This method helps us to study the branching of the molecules in BR and SBR, which influences how easy they are to process and how well they perform at the product level. We found that BR and SBR behave differently due to their unique branching patterns. This study provides a way to identify the branching in these rubbers, which can help in designing better rubber compounds for specific needs.

Introduction

Synthetic rubbers, such as Butadiene Rubber (BR) and Styrene-Butadiene Rubber (SBR), are essential materials in a wide array of industrial applications, from tyre production to sealing and insulation solutions. Their extensive usage is due to their superior mechanical properties, including elasticity, strength and resistance to wear at a wide range of temperatures. These properties are profoundly influenced by the molecular structure of the rubbers, particularly the degree and type of branching within the polymer chains. Branching, which involves the formation of side chains attached to the main polymer backbone, plays a crucial role in determining the viscoelastic behavior, processability and overall performance of these materials. The extent of branching is significantly influenced by the chemical characteristics of the free radicals or organometallic catalysts that initiate the polymerization reaction [1]. A thorough understanding of their branching characteristics is vital to tailor the properties of BR and SBR for specific applications. Highly branched polymers, for example, may exhibit different stress-relaxation behaviors compared to their linear counterparts, influencing the durability and mechanical stability of the rubber. Conventional analytical techniques, such as Gel Permeation Chromatography (GPC) [2] and Nuclear Magnetic Resonance (NMR) spectroscopy [3], provide valuable insights into the molecular weight distribution and chemical composition of polymers. The determination of functional group can be identified by the Fourier Transform Spectroscopy technique (FT-IR) for the polymer [4]. However, these methods cannot often fully characterize the dynamic mechanical properties of rubbers, which are critical for predicting their performance under real-world conditions.

Advanced analytical tools, like the Rubber Process Analyzer (RPA), address these limitations by providing a detailed evaluation of the viscoelastic properties of rubber compounds [5]. One of the key tests conducted with the RPA is the phase angle vs. frequency analysis. The phase angle, which measures the delay between applied stress and the resulting strain, offers valuable insights into the material's viscoelastic nature. By examining the phase angle over a range of frequencies, researchers can gain a comprehensive understanding of the material's response to varying dynamic conditions, uncovering crucial details about its molecular architecture and branching. In this study, we use the RPA to carry out an in-depth phase angle vs. frequency analysis of BR and SBR. Our goal is to identify the branching characteristics of these polymers. Detecting branching structures in BR is challenging with existing techniques. This phase angle study offers a significant advantage to researchers, providing an easy method for comparing different polymers. The results from this research will provide insights into the distinct phase angle behaviors of BR and SBR, expected to be related to their unique branching structures. By offering a thorough evaluation of these materials, this study aims to establish a solid foundation for the improved design and development of rubber compounds. These advancements will facilitate the creation of customized rubber products that meet specific performance criteria, thereby enhancing the functional capabilities of synthetic rubbers across various industrial sectors.

Experimentation

In this research, we studied three different grades of Butadiene Rubber (BR) catalyzed by Lithium (Li-BR), Nickel (Ni-BR) and Neodymium (Nd-BR), as well as various types of Emulsion Styrene-Butadiene Rubber (ESBR), including ESBR 1502, ESBR 1712, ESBR 1723 and ESBR 1739. The Ni-BR, which has a high 1,4-cis content and a moderate degree of branching, was provided by Reliance Industries, Hazira, India, along with ESBR 1502, with a styrene content of 23.4%, ESBR 1712, which is oil-extended with a styrene content of 23.4% and ESBR 1739, which is oil-extended with a styrene content of 40.0%. The Nd-BR was sourced from Arlanxeo, USA and is characterized by a very high 1,4-cis content, very low 1,2-vinyl content, a relatively narrow molecular weight distribution and a low degree of branching. The Li-BR was obtained from Versalis, USA, with a very low 1,4-cis content, with a linear structure and ESBR 1723, which is oil-extended with a styrene content of 23.5%, was provided by Indian Synthetic Rubber Limited (ISRL), Panipat, India. During the frequency sweep, the Rubber Process Analyzer (RPA) varied the frequency from 0.1 to 314 radians per second (rad/s) of the applied oscillatory strain at a constant strain of 10% and a temperature of 100 °C. The RPA measured the corresponding phase angle, providing insights into how the viscoelastic properties of the polymers change with frequency. This approach helps in understanding the behavior of the polymers under different dynamic conditions.

Results & Discussion

The phase angle observed at low frequencies is a vital indicator of polymer branching. A higher phase angle at these frequencies implies lower branching, reflecting greater chain mobility and higher energy dissipation. Conversely, a lower phase angle at low frequencies indicates increased branching, which restricts chain movement and enhances energy storage. Understanding this relationship is crucial for accurately characterizing and designing polymers with tailored viscoelastic properties for diverse applications. The phase angle data at lower frequencies for BR and ESBR is presented in Table 1. From Figure 1, Lithium-based Butadiene Rubber (BR) exhibits the lowest branching and is more linear due to the controlled, chain-end-type polymerization promoted by lithium catalysts. Neodymium-based BR, with a more complex polymerization mechanism, produces moderate branching, with a medium phase angle resulting in a mix of linear and branched structures that offer a balance between elasticity and processability. Nickel-based BR shows the highest degree of branching with the least phase angle, fostering extensive chain branching and cross-linking that enhances the material's toughness and elasticity.

Table 1: Phase angle (°) data at low-frequency (BR & SBR).

Frequency (rad/s)	Nd-BR	Ni-BR	Li-BR	ESBR 1502	ESBR 1712	ESBR 1723	ESBR 1739
0.1	46.5	38.5	50.4	35.8	34.8	34.5	34.2

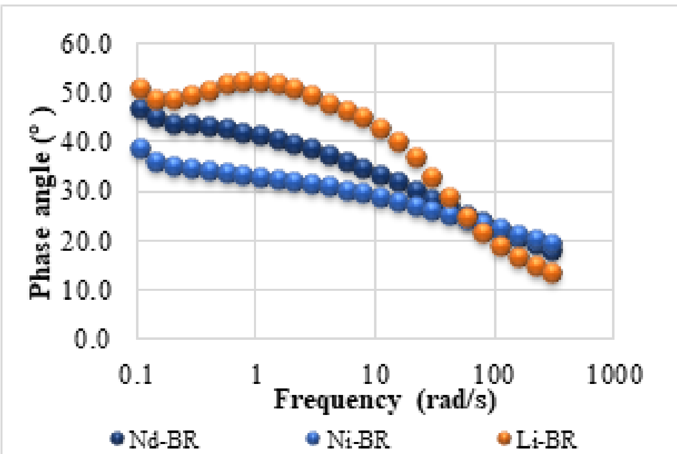

Figure 1: Branching study-BR phase angle vs frequency study.

Similarly, Figure 2 illustrates that the branching in different SBR types is significantly influenced by their specific polymerization methods and the additives used. SBR 1502, which is produced with fewer additives, has the simplest and most linear structure, resulting in the highest phase angle. In contrast, SBR 1739, which involves the use of more branching agents and more complex production processes, exhibits the highest degree of branching and consequently the lowest phase angle at lower frequencies. Despite the structural similarities among the 1700 series, SBR 1739 stands out due to its greater complexity and higher branching with the highest Molecular weight [6]. The findings of the phase angle versus frequency study are consistent with the Van Gurp-Palmen Plot, which is commonly used to illustrate the relationship between phase angle and complex modulus in rheological analysis [7,8].

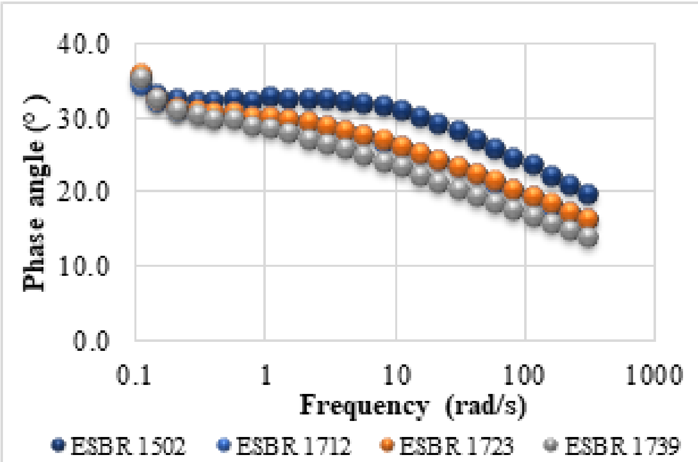

Figure 2: Branching study-SBR phase angle vs frequency study.

Conclusion

In conclusion, the phase angle at low frequencies from RPA analysis is a critical measure of polymer branching, illustrating the impact of different polymerization techniques and catalysts on chain dynamics and energy dissipation. Lithium-based butadiene rubber exhibits minimal branching, leading to a more linear structure [6], whereas neodymium-based BR achieves a blend of linear and branched chains, striking a balance between elasticity and processability. In contrast, nickel-based BR shows significant branching, enhancing both toughness and elasticity. The varying degrees of branching in different SBR types, influenced by their specific production methods and the use of additives, highlight the necessity of understanding these relationships to design polymers with tailored viscoelastic properties for targeted applications.

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References

1. Poddubnyi IY, Ehrenburg EG (1958) Branching in macromolecules of different synthetic rubbers. J Polym Sci 29(120): 605-619.
2. Drott EE, Mendelson RA (1970) Determination of polymer branching with gel-permeation chromatography. J Polym Sci A-2 Polym Phys 8(8): 1361-1371.
3. Chen A, Wu D, Johnson CS (1995) Determination of molecular weight distributions for polymers by diffusion-ordered NMR. Journal of the American Chemical Society 117(30): 7965-7970.
4. Berridi MJ, González N, Mugica A, Bernicot C (2006) Pyrolysis-FTIR and TGA techniques as tools in the characterization of blends of natural rubber and SBR. Thermochimica Acta 444(1): 65-70.
5. Müllner HW, Jäger A, Aigner EG, Eberhardsteiner J (2008) Experimental identification of viscoelastic properties of rubber compounds by means of torsional rheometry. Meccanica 43: 327-337.
6. Kraus G, Stacy CJ (1972) Molecular weight and long-chain branching distributions of some polybutadienes and styrene-butadiene rubbers. Determination by GPC and dilute solution viscometry. J Polym Sci A-2 Polym Phys 10(4): 657-672.
7. Trinkle S, Friedrich C (2001) Van gurp-palmen-plot: A way to characterize polydispersity of linear polymers. Rheol Acta 40: 322-328.
8. Trinkle S, Walter P, Friedrich C (2002) Van gurp-palmen plot II-classification of long chain branched polymers by their topology. Rheol Acta 41: 103-113.

