LATEX VISCOELASTICITY: A RECENT LITERATURE REVIEW THAT ADDRESSES THE MOST USED TREATMENT METHODS

VISCOELASTICIDADE DO LÁTEX: UMA REVISÃO RECENTE DA LITERATURA QUE ABORDA OS MÉTODOS DE TRATAMENTO MAIS UTILIZADOS

VISCOELASTICIDAD DEL LÁTEX: UNA REVISIÓN BIBLIOGRÁFICA RECIENTE QUE ABORDA LOS MÉTODOS DE TRATAMIENTO MÁS UTILIZADOS

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ABSTRACT

Rubber is an important material that by ignorance of its properties has spent a lot of time without any relevant utility. After presenting its physical and mechanical properties, it became present in the composition of many industrial products, mainly due to its ability to recover from deformation. However, understanding the viscoelastic behavior in the most varied applications and medium is extremely necessary for better application of this product. Therefore, this work aims to discuss the viscoelasticity of latex through a study of articles found in the literature, seeking to understand the relationship of the variables found with the products studied. The publications were selected from a search in the databases (CAPES Journals, Scielo and Google Scholar) in the period from 2017 to 2021. The results of the searches culminated in thirteen articles related to the property of rubber viscoelasticity and, after being analyzed, it was possible to verify that the
studies investigated the viscoelastic behavior, highlighting that the most used evaluation method to obtain the viscoelastic response was the rheometer.

**Keywords:** Viscoelasticity; latex; rubber.

**RESUMO**
A borracha é um importante material que, por desconhecimento de suas propriedades, passou muito tempo sem qualquer utilidade relevante. Após apresentar suas propriedades físicas e mecânicas, passou a estar presente na composição de muitos produtos industriais, principalmente devido a sua capacidade de se recuperar de deformações. Entretanto, entender o comportamento viscoelástico nas mais variadas aplicações e meios é extremamente necessário para uma melhor aplicação deste produto. Portanto, este trabalho tem como objetivo discutir a viscoelasticidade do látex através de um estudo de artigos encontrados na literatura, buscando entender a relação das variáveis encontradas com os produtos estudados. As publicações foram selecionadas a partir de uma busca nas bases de dados (Periódicos CAPES, Scielo e Google Scholar) no período de 2017 a 2021. Os resultados das buscas culminaram em treze artigos relacionados à propriedade de viscoelasticidade da borracha e, após serem analisados, foi possível verificar que os estudos investigaram o comportamento viscoelástico, destacando que o método de avaliação mais utilizado para obtenção da resposta viscoelástica foi o reômetro.

**Palavras-chave:** Viscoelasticidade; látex; borracha.

**RESUMEN**
El caucho es un importante material que por desconocimiento de sus propiedades ha pasado mucho tiempo sin tener ninguna utilidad relevante. Después de presentar sus propiedades físicas y mecánicas, pasó a estar presente en la composición de muchos productos industriales, principalmente debido a su capacidad de recuperación de la deformación. Sin embargo, la comprensión del comportamiento viscoelástico en las más variadas aplicaciones y medios es extremadamente necesaria para una mejor aplicación de este producto. Por lo tanto, este trabajo tiene como objetivo discutir la viscoelasticidad del látex a través de un estudio de artículos encontrados en la literatura, buscando entender la relación de las variables encontradas con los productos estudiados. Las publicaciones fueron seleccionadas a partir de una búsqueda en las bases de datos (CAPES Journals, Scielo y Google Scholar) en el período de 2017 a 2021. Los resultados de las búsquedas culminaron en trece artículos relacionados con la propiedad de viscoelasticidad del caucho y, después de ser analizados, fue posible verificar que los estudios investigaron el comportamiento viscoelástico, destacando que el método de evaluación más utilizado para obtener la respuesta viscoelástica fue el reômetro.

**Palabras clave:** Viscoelasticidad; látex; caucho.

**1. Introduction**

Rubber is a material used in a wide range of industrial applications, such as in the manufacture of tires, surgical gloves, condoms, pacifiers, mattresses, soles, vegetable leather, footwear and others [1, 2, 3]. This fact is due to the main
characteristic of this elastomer, viscoelasticity, because this characteristic provides two main contributions: restoration stress proportional to deformation and damping stress proportional to the deformation rate [4, 5, 6]. On the other hand, the vast application of elastomers generates the need for studies aimed at the knowledge of viscoelastic behavior in various means and practical situations.

Many factors can influence the viscoelasticity of rubber, such as conformation, additives, particle size, temperature, vulcanization, and mobility [5, 7, 8, 9]. Thus, the knowledge of viscoelastic properties can be obtained by performing dynamic experiments in a range of time, temperature or frequency [10]. Therefore, the knowledge of the viscoelastic profile is very important for the prediction of a rubber processing.

The objective of this work is to promote the discussion of latex viscoelasticity through a study of selected articles in the literature, seeking to understand the relationship of the variables found with the products studied, in order to provide information for the best development of rubber products.

This article is structured as well: The experimental procedure used in the study is presented in section 2. The analysis of rubber viscoelasticity articles is presented and discussed in Section 3. In section 4, the last being, the final considerations are presented.

2. Methodology

Thirteen articles on the viscoelasticity of rubbers, published in scientific journals, were randomly selected from a bibliographic research in the following databases: capes, scielo and google scholar journals. In these studies, the following terms were used: viscoelasticity, latex, rubber, elastomer and viscoelastic property. The criterion applied as a prerequisite for the selection of scientific articles was: publication of articles between the years 2017 to 2021. After the selection of the articles, a thorough reading was performed, from which the main information of the texts was extracted and analyzed and later taken to discussion.
3. Results and Discussion

Of the thirteen articles selected for evaluation, twelve worked in their investigations on natural rubber and, depending on the application of this rubber, studies were done considering the addition of components in this rubber, such as: carbon black, hybrid graphene structure, silica filler, nylon short fiber and nanodiamond, according to Table 1. Another important point is the description of the methods of viscoelasticity evaluation. It can be observed that the rheometer was the most widely adopted evaluation method in the researches, being present in seven of the selected articles.

Table 1. Articles from 2017 to 2021 related to rubber viscoelasticity.

<table>
<thead>
<tr>
<th>Order</th>
<th>Material</th>
<th>Method of evaluation of viscoelasticity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Natural rubber and ingredients</td>
<td>Fatigue resistance</td>
<td>[5]</td>
</tr>
<tr>
<td>2</td>
<td>Vulcanized rubber with carbon black</td>
<td>Dynamic tests (rheometer)</td>
<td>[6]</td>
</tr>
<tr>
<td>3</td>
<td>Natural rubber</td>
<td>Voltage relaxation (rheometer)</td>
<td>[11]</td>
</tr>
<tr>
<td>4</td>
<td>Natural rubber filled with hybrid structure of graphene and carbon black</td>
<td>Axial stress test</td>
<td>[8]</td>
</tr>
<tr>
<td>5</td>
<td>Natural rubber</td>
<td>Shear traction</td>
<td>[12]</td>
</tr>
<tr>
<td>6</td>
<td>Natural rubber</td>
<td>Rubber process analyzer</td>
<td>[3]</td>
</tr>
<tr>
<td>7</td>
<td>Natural rubber and silicone rubber</td>
<td>Rubber process analyzer</td>
<td>[13]</td>
</tr>
<tr>
<td>8</td>
<td>Rubber with silica filler</td>
<td>Mechanical analysis by shear (rheometer) and fluency</td>
<td>[14]</td>
</tr>
<tr>
<td>9</td>
<td>Natural rubber</td>
<td>Scans of deformation and dynamic mechanical analyzer (rheometer)</td>
<td>[9]</td>
</tr>
<tr>
<td>10</td>
<td>Natural rubber filled with precipitated silica and short nylon fiber</td>
<td>Dynamic tests (rheometer)</td>
<td>[15]</td>
</tr>
<tr>
<td>11</td>
<td>Natural rubber nanodiamond composite</td>
<td>Dynamic tests (rheometer)</td>
<td>[16]</td>
</tr>
<tr>
<td>12</td>
<td>Nitrile rubber</td>
<td>Simple shear pretension and hydrostatic pressure</td>
<td>[17]</td>
</tr>
<tr>
<td>13</td>
<td>Natural rubber filled with silica</td>
<td>Dynamic mechanical analyzer (rheometer)</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Source: Elaborated by the author, 2022.

Three articles were found, items 1, 2 and 8 of Table 1, which reported in their studies rubbers for automotive use. Article 1 [5] investigated the viscoelastic properties of natural rubber, filled with the elements shown in Table 2, generating the two compounds A and B. The rubber used in this study is used in a tire tread band, which is exposed to high temperatures (range from 70 °C to 80 °C during operating conditions), and this is investigated the variation of viscoelastic property due to fatigue in this temperature range.
Puma-Araújo et al. [6] (Article 2-Table 1) studied viscoelastic rubber supports used in suspensions of vehicles with electric motors on wheels, which aimed to represent a viscoelastic model suitable for the selection of rubber materials for bushings as support and insulation elements for vehicle suspensions. For this, they characterized vulcanized rubber with carbon black. The rubber supports of viscoelastic material were proposed to support the mass of the engine in the wheel within the non-suspended mass of the vehicle. In Article 8 [14] the linear and nonlinear viscoelastic properties in rubber filled with silica for tire tread were studied. The authors discussed the difference in nonlinear response between the modes of traction and oscillatory shear and analyzed relaxation data of deformation (fluency) for the same systems.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Composition (parts per hundred rubber)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Compound A</td>
</tr>
<tr>
<td>Natural rubber</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black (HAF-HS)</td>
<td>50</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>2.5</td>
</tr>
<tr>
<td>Sorric acid</td>
<td>2.5</td>
</tr>
<tr>
<td>Antidetrills</td>
<td>2.25</td>
</tr>
<tr>
<td>Sulfur accelerator ratio</td>
<td>4</td>
</tr>
</tbody>
</table>

Source: RANGARAJAN & RAMARATHNAM, 2021 [5].

Like studies 1 and 2, study 4 [8] investigated the viscoelastic and fatigue properties of natural rubber composites filled with carbon black, but was also added to the composite hybrid graphene structure. Article 11 [16] investigated the distribution of nanodiamond within the natural rubber nanomatrix and related to mechanical and viscoelastic properties.

The research conducted in 10 [15] described the linear rheology of natural rubber compounds filled with silica, short nylon fiber or both. As well as Article 13 [10] investigated the viscoelastic behavior through the correlation of shear with elongation test in natural rubber composites filled with silica. The research of article 7 [13] studied the relationship between the properties of crack propagation by dynamic fatigue and viscoelasticity of natural rubber/silicone rubber composites.

Articles 6 and 9 evaluated the viscoelasticity of the materials correlating
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...the sizes of the rubber particles. Article 3 [11] showed the influence of planting climate and storage time on the thermal and viscoelastic properties of natural rubber, and non-vulcanized natural rubber was collected in the period of two years and seven months. Finally, a single unnatural rubber article, Article 12 [17], was found, in which the direct measurement of the high frequency viscoelastic properties of the nihilic rubber was investigated.

The remometer was the most applied method in the researches investigated, being present in 7 articles. In Article 2 [6] the authors characterized rubber through dynamic tests, in which they used the Hybrid Rheometer Discovery HR 2TM (Waters Corporation, New Castle, DE, USA) defined for a minimum oscillation force of 0.03 N and a maximum axial force of 50 N. This device is capable of recording with displacement resolution of 20 nm in a range of 0.1 to 16 Hz. A parallel plate compression accessory was used to apply cyclic loading to the sample with a preload of 15 N. Figure 1 presents images of the experimental configuration described.

Figure 1. Images of the experimental configuration (a) Hybrid Rheometer Discovery HR 2TM; (b) Sample installed in the test machine [6].

In Article 3 [11] a parallel plate rheometer and a cone rheometer and plates of varied geometries were used, in which to perform stress relaxation measurements were made constant shear deformations at 210 °C and 250 °C, in order to understand how high processing temperatures can change the
viscoelastic behavior. Five repetitions were performed to ensure repeatability. In Article 8 [14] the researchers used the Metravib dynamic mechanical analysis instrument (DMA) in shear mode and scans of strain in oscillatory stress mode, using a Q800 DMA instrument produced by TA Instruments.

Sirling et al. [9], Article 9, showed that the viscoelastic properties of each uncured rubber sample were studied by deformation and frequency scans, using the Alpha 2000 RPA device at 80 °C. The dynamic thermomechanical properties of each vulcanized rubber sample were measured using a Gabo Plexer 25 N (DMA) dynamic mechanical analyzer, according to ISO 4664-112.

To obtain the results of the research carried out in article 10 [15] a rheometer controlled by deformation (ARES-G2, TA Instrument, USA) was used to measure the dynamic rheological responses of uncured compounds at 100 °C, using plate-plate geometry with a serrated surface texture to avoid slipping, and frequency scans of 100 to 0.0158 rad.s\(^{-1}\) were performed at 0.1% of the dynamic strain amplitude located in the linearity regime.

In article 11 [16] the dynamic mechanical properties were measured using the Anton Paar Physica MCR 301 rheometer (12 mm in diameter) and with parallel plate geometry. The angular frequency range was from 0.1 to 100 rad s\(^{-1}\) and the measurements were obtained between −70 °C and 130 °C. For all measurements, the deformation amplitude was in the linear viscoelasticity region. Measurements for the rubberized plateau were obtained at 25 °C.

In the research conducted in Article 13 [10], the results were acquired by a frequency scanning method at different temperatures (40 °C, 70 °C and 100 °C), using a dynamic mechanical analyzer and a reometer without rotor, RPA, in an attempt to establish a correlation between the two.

Other methods of viscoelasticity evaluation have been found in the literature. A method adopted by the authors of article 1 [5] was through an experimental procedure involving resistance tests, conducted in an FM-21 electric bending machine (Gordon Solutions, India) in controlled displacement mode (Fig. 2) and with similar previous experiments performed at room temperature [18].
In the study conducted in Article 4 [8], as well as in the previous work, a test sample in the form of a dumbbell was used (the average thickness of the narrow part of the sample was 1 mm and the experimental length was 10 mm). However, the test adopted was axial stress in dynamic mechanical analyzer (TA instrument, DMA Q850, USA), load accuracy of 0.1 mN, displacement accuracy of 0.5 μm and temperature accuracy of 0.5 ºC. In article 12 [17] the viscoelasticity of the rubber was measured from simple shear and hydrostatic pressure at frequencies from 200 Hz to 2000 Hz, under pretensioning of shear and precompression.

The researchers of articles 6 and 7 evaluated viscoelasticity using rubber process analyzer (RPA). In Article 6 [3] the samples (5 g) evaluated form submitted to strain and frequency scanning tests, using an RPA 2000 (Alpha, USA) at 80 ºC. In Article 7 [13] we evaluated the dependence of the amplitude of the deformation of viscoelastic parameters in the compounds, measured by the rpa rubber processing analyzer (RPA 2000, Alpha technology Co., Ltd., America) with a deformation range of 0.28% - 400% and frequency from 1 Hz to 100 ºC. After the first scan of strains, all compounds were vulcanized at 170 ºC. Then, the vulcanized were conducted by scan of deformation with a range of 0.28 % - 40%, frequency of 10 Hz and temperature of 60 ºC.
The results of articles 1, 2 and 8 generated answers to problems found in rubber manufacturing in the automotive industry. The experimental results of Article 1 [5] suggest a deterioration of the stiffness of the equilibrium network, due exclusively to the load of fatigue and that the magnitude of the variation of the parameters of the test specimens tested at high temperature was similar to that of the specimens tested at room temperature. The 70 ºC fatigue test resulted in reduced service life, however, high temperature fatigue showed no permanent effect on stress-strain response. The results also indicate that stiffness degradation is not an indicator of fatigue-induced damage. However, no trend was found suggestive of the effect of the damage on viscoelasticity [5].

In study 2 by Puma-Araujo et al. [6] it was found that the rheological parameters were adjusted from experiments and included in the suspension by means of a geometric factor. This ideal selection of geometric factors of the bushing has led to mounting solutions that meet the mechanical and thermal constraints of the design.

In Article 8 [14] the results demonstrated that for rubber friction on road surfaces, a direct measurement of the viscoelastic modulus in response to the applied oscillating deformation is the best approach, since pulsating deformations acting on the rubber surface during slippage on the surface of hard and rough substrate (e.g., a road) are similar to oscillatory deformations in the DMA experiment.

However, tensile measurements require pre-voltage that breaks the fill network, which will affect the effective module. In rubber friction experiments, the roughness of the road glides along the rubber surface and there is very little pre-tension. This suggests that the shear module (obtained without pre-deformation) is probably better than the modulus obtained in the tension with pre-deformation. An even better method involves bearing friction experiments, in which the associated deformations are very similar when roughness slides over the rubber surface.

Regarding the additives added to natural rubber, articles 4, 7, 10, 11 and 13 reached the following conclusions, related to viscoelasticity. In study 4 [8] the results show that the dynamic viscoelastic analysis of different types of rubber
composites with doped graphene can significantly reduce the loss of composites in a single dynamic loading cycle. Graphene with the interface modified graphene hybrid structure has better viscoelasticity than carbon black filled natural rubber composites. The internal viscosity of the nanocomposites increases significantly with the characteristics of the interface of the fillers, hindering the fluidity of the rubber matrix.

The authors of research 7 [13] observed that with the increase of the silicone rubber fraction, the composite showed a lower rate of crack growth, therefore, more energy dissipation occurred in the linear viscoelastic region in front of the crack tip, which consumed part of the energy for crack growth.

In article 10 [15] the researchers concluded that both precipitated silica and short nylon fiber induce the apparent transition from liquid to solid. Despite the dimensional differences in the two loads, this transition can be well explained by the time concentration superposition principle. Filling invariably slows down the mobile phase dynamics of rubber, while the coexistence of two types of filler can accelerate the liquid-solid transition. However, the presence of one filler type does not influence the strengthening and dissipation effects associated with another filler type.

The research developed in article 11 [16] concluded that the structure of the nanomatrix with deproteinized natural rubber has compacted nanodiamond agglutinates of about 10 nm. The formation of the nanodiamond nanomatrix structure contributed a lot to increase the mechanical and viscoelastic properties. In article 13 [10] the conclusion was that the dynamic mechanical properties of rubber compounds can be determined even during curing. The silane coupling agent, bis (3-triethoxysilylpropyl tetrasulfide) in the rubber corresponded to a behavior in the constant linear viscoelastic region. Complex viscosity variation with frequency shows shear dilution behavior, regardless of filler content.

Previous studies that investigated natural rubber compositions with Ethylene Vinyl Acetate (EVA) concluded that the non-vulcanized compositions had their viscosity increased by the addition of increasing contents of this polymer. After vulcanization these compositions showed lower elasticity than pure natural rubber [19]. Another composition found in a past study is butyl
acrylate (BA)/acrylic acid/2-hydroxyethyl methacrylate latex, in which they concluded that shear strength can be significantly improved without sacrificing adhesion and peel strength, improving entanglement between composite chains [21].

Another important factor in investigating the behavior of rubber viscoelasticity is the size of the particles (articles 6 and 9). The authors of article 6 [3] concluded that the 70/30 blend (large particles/small particles) presented the best resistance to thermal aging among the vulcanized. This suggested that the mixing ratios of the large particle and small particle contents were adjustable to improve the desirable properties of the rubber products of interest, both green and cured. The viscoelastic and mechanical properties of the large-particle and small-particle rubbers revealed that, in unvulcanized samples, both the mechanical strength and elasticity of the large-particle rubber were better than those of the small-particle rubber.

Sriring et al. [9] (article 9) concluded that the unvulcanized large particle rubber showed better viscoelastic and mechanical properties than the small particle rubber counterpart, this is due to the natural branching network structure of the aggregation of the phospholipid ends, which was stronger than that of the branch points around the proteins found in large-particle rubber. After vulcanization, small particle vulcanizate performed better in all respects. This can be explained by the accelerating effect of proteins attached to the leading end of the rubber chains of small particles in the crosslinking process during vulcanization.

A previous study on particle size in the final properties of the viscoelastic film was found in the literature, in which it was concluded that the smaller the size of the hard particles, the better the mechanical improvement of the viscoelastic properties of the film [20].

In article 3 [11] the viscoelasticity of rubber in its planting process was investigated, and the authors found that the increase in temperature increases the free volume within the material, improving the mobility at the molecular level of natural rubber. Higher processing temperatures translate to decreased relaxation times and decreased overall stresses experienced by the sample. The
ultrasound study found that an increase in monthly rainfall caused an increase in the spring constant of the material at the frequency of 10 MHz, and the crystallization study found that the amount of crystallization decreased with increasing rainfall, remaining relatively constant if the rain was falling within the recommended amount for the tree.

Regarding the investigation of rubber viscosity, a previous study evaluated the performance of 12 combinations of three panel clones (PB 311, PB 314 and RRIM 600) with four crown clones (F 4512, MDF 180, IAN 6158 and IAN 6543) rubber, in which they concluded that the panel clone PB 314 has the best rubber quality with greater retention of plasticity and Mooney viscosity [22].

In article 5, Schapery [12] investigated the effect of global viscoelasticity on rubber friction with Schallamach waves. The author found that global viscoelasticity limits the maximum slip velocity and the minimum wavelength for which waves can exist and, as expected, increases the friction force. The main effect of global viscoelasticity is to place an upper bound on slip velocity on Schallamach waves and a lower bound on wavelength. Above this speed, the Schallamach waves become unstable because, with a small increment of the sliding speed, it exceeds the required force. Below this critical velocity, the prediction of the effect of slip velocity on wavelength and wave velocity is even more in agreement with the experiment than without global viscoelasticity in the model.

Finally, in article 12 [17], the study carried out with nitrile rubber showed in its results that the hydrostatic pressure had a much greater influence than the pre-shear stress. Hydrostatic pressure should be considered as a more essential parameter than stretching or deformation in this material.

4. Conclusion

In this article, several works were reviewed regarding investigations on the viscoelastic property of rubber. Thirteen articles included in the years 2016 to 2021 were selected. It was concluded that most current articles portray in their respective research on natural rubber, with emphasis on studies related to products in the automotive industry. It was observed that in carbon black, the
hybrid structure of graphene, silica filler, nylon short fiber and nanodiamond were the most studied components in rubber compositions in current studies. In addition, they showed better viscoelastic results for large rubber particles. Finally, it was found that the rheometer was the most used evaluation method for the investigation of viscoelasticity, performed mainly by dynamic tests.

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