

# The Effectiveness of the Havriliak-Negami Model in Predicting the Master Curves of the Asphalt Blends with SBS Triblock Copolymer and Organic-Montmorillonite at Different Temperatures and Frequencies

# María Ángeles Vargas-Hernández<sup>1\*</sup>, Miguel Ángel Vargas<sup>2</sup>, Pedro R. García-Morán<sup>3</sup>, Humberto Vázquez-Torres<sup>4\*</sup>

<sup>1</sup>División de Ingeniería Química y Bioquímica, TecNM—Tecnológico de Estudios Superiores de Ecatepec, Edo. de México, México

<sup>2</sup>Facultad de Química, Universidad Nacional Autonóma de México, Cd. de México, México

<sup>3</sup>Facultad de Ciencias Básicas Ingeniería y Tecnología, Universidad Autónoma de Tlaxcala, Tlaxcala, México

<sup>4</sup>Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Cd. de México, México

Email: \*maria\_vargas@tese.edu.mx, \*hvto@xanum.uam.mx

How to cite this paper: Vargas-Hernández, M.Á., Vargas, M.Á., García-Morán, P.R. and Vázquez-Torres, H. (2024) The Effectiveness of the Havriliak-Negami Model in Predicting the Master Curves of the Asphalt Blends with SBS Triblock Copolymer and Organic-Montmorillonite at Different Temperatures and Frequencies. *Journal of Materials Science and Chemical Engineering*, **12**, 23-39.

https://doi.org/10.4236/msce.2024.127003

**Received:** June 9, 2024 **Accepted:** July 27, 2024 **Published:** July 30, 2024

Copyright © 2024 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

http://creativecommons.org/licenses/by/4.0/

## Abstract

The dynamic viscoelastic properties of asphalt AC-20 and its composites with Organic-Montmorillonite clay (OMMt) and SBS were modeled using the empirical Havriliak-Negami (HN) model, based on linear viscoelastic theory (LVE). The HN parameters, a,  $\beta$ ,  $G_e$ ,  $G_g$  and  $\tau_{\rm HN}$  were determined by solving the HN equation across various temperatures and frequencies. The HN model successfully predicted the rheological behavior of the asphalt and its blends within the temperature range of 25°C - 40°C. However, deviations occurred between 40°C - 75°C, where the glass transition temperature  $T_g$  of the asphalt components and the SBS polymer are located, rendering the HN model ineffective for predicting the dynamic viscoelastic properties of composites containing OMMt under these conditions. Yet, the prediction error of the HN model dropped to 2.28% - 2.81% for asphalt and its mixtures at 100°C, a temperature exceeding the  $T_g$  values of both polymer and asphalt, where the mixtures exhibited a liquid-like behavior. The exponent a and the relaxation time increased with temperature across all systems. Incorporating OMMt clay into the asphalt blends significantly enhanced the relaxation dynamics of the resulting composites.

#### **Keywords**

Asphalt, Blends, Master Curve, Linear Viscoelasticity, Havriliak-Negami Model

# **1. Introduction**

One of the main research tasks in the construction industry is to develop new asphalt blends with an optimal composition of raw materials that function under acceptable conditions and exhibit enhanced properties, such as heat and aging resistance [1]. Asphalt pavement undergoes severe service conditions, including repeated vehicle loading and complex environmental changes, leading to cracking, rutting, and other structural damage [2]. Therefore, the evaluation and design of asphalt mixtures are influenced by the local environmental temperature and traffic loading [3]. Mathematical modeling optimizes and predicts the quality and performance of asphalt, a task made challenging by the blends' high nonlinearity and anomalous property changes. Several models, including those from Maxwell, Kelvin-Voigt, generalized Maxwell, Huet, and standard linear (SLM), describe the rheological behavior of asphalt materials using various approaches [1] [4]. The Havriliak-Negami (HN) model integrates a distribution of the single relaxation time, the broadness of the Cole-Cole model, and the asymmetry of the Davidson-Cole model [4]. It is highly valuable for predicting the viscoelastic properties of rubber-like materials, such as polymers, in engineering applications due to its simplicity and minimal parameter requirements [4] [5]. Studies on the HN model's parameters for neat asphalt and asphalt mixtures with materials such as ceramics, clay, silica, rutile, alumina nanoparticles, and fiber reinforcements are scarce [6] [7]. The addition of fillers or clays to polymers and asphalt matrices affects the relaxation of the macromolecular chains due to strong interfacial interactions. The interaction between polymers and particles is crucial to control because nanoparticles delay the dynamics of macromolecular chains. In this context, the HN model may not align well with experimental data when describing the dynamic viscoelastic properties of asphalt binders and could be limited in accurately representing the dynamic viscoelastic properties of viscoelastic materials. Conversely, asphalt performance can be determined through rheological characterization and the time-temperature superposition principle (TTSP). TTSP is used to construct master curves of various response functions (G', G'',  $G^*$ , etc.) of asphalt and its blends under experimental conditions of linear viscoelastic behavior (LVE) [5]. In the case of thermorheologically simple materials, the time-temperature shift factor  $(a_r)$  is utilized to superpose all viscoelastic functions.

The goal of this study is to assess the suitability of the HN model for complex materials like asphalt and its mixtures with polymer styrene-butadiene-styrene (SBS) and Organic-Montmorillonite (OMMt) clay at various temperatures (25°C,

40°C, 60°C, 75°C, and 100°C) across a broad frequency range. To this end, rheological tests in the linear viscoelastic region were performed on asphalt and its blends. Master curves of test data were constructed for four different asphalt binders. Parameters ( $G_e$ ,  $G_g$ ,  $\tau$ ,  $\alpha$  and  $\beta$ ) were determined by fitting the experimental data to the HN model, and the potential interactions between clay particles, polymer, and asphalt in the blends were analyzed.

### 2. Theory Section

## 2.1. Havriliak-Negami Model

Storage modulus, viscous modulus, and phase angle, obtained from experimental tests, characterize the LVE behavior of asphalt concrete [8]. The complex shear modulus is:

$$G^* = G' + iG'' \tag{1}$$

The measure of damping efficiency, also known as the loss factor, is:

Loss factor  $\tan \delta = G'' / G'$  (2)

where  $\delta$  is the phase angle in the complex plane.

Havriliak-Negami model is given in the following equation [9]:

$$G*(\omega) = \frac{G_e - G_g}{\left[1 + (i\omega\tau)^{\alpha}\right]^{\beta}} + G_g$$
(3)

where  $G_e$  represents the equilibrium modulus,  $G_g$  represents the glassy modulus,  $\tau$  is the single relaxation time that controls the horizontal position of each component of the complex modulus along the frequency axis;  $\alpha$  controls the amplitude of the relaxation spectrum of the loss peak, and  $\beta$  governs the asymmetry of the loss peak [7]. The parameters  $\alpha$  and  $\beta$  can take values between 0 and 1 [10]. The glassy modulus has a high-frequency limit value,  $G_g$  or unrelaxed modulus, and a low-frequency limit value  $G_e$ , or relaxed modulus. A transition occurs between these two limit values in a range of frequencies centered at  $\omega_{\phi}$  showing a peak. The process is relaxed; therefore, it is convenient to define a relaxation time ( $\tau$ ), associated with the central frequency [11]:

$$=\frac{1}{\omega_0} \tag{4}$$

The three independent parameters ( $G_g$ ,  $G_e$ , and  $\tau$ ) define a relaxation process. According to De Moivre's theorem, the storage modulus and loss modulus can be analytically solved from the HN model, as shown below [9]:

τ

$$G' = G_g + \frac{\left(G_e - G_g\right)\cos\left(\beta\theta\right)}{\left[1 + 2\omega^{\alpha}\tau^{\alpha}\cos\left(\alpha\beta/2\right) + \omega^{2\alpha}\tau^{2\alpha}\right]^{\beta/2}}$$
(5)

$$G'' = \frac{\left(G_g - G_e\right)\sin\left(\beta\theta\right)}{\left[1 + 2\omega^{\alpha}\tau^{\alpha}\cos\left(\alpha\beta/2\right) + \omega^{2\alpha}\tau^{2\alpha}\right]^{\beta/2}}$$
(6)

$$\theta = a \operatorname{rctan}\left(\frac{\omega^{\alpha} \tau^{\alpha} \sin\left(\alpha\pi\right)}{\left[1 + \omega^{\alpha} \tau^{\alpha} \cos\left(\alpha\beta/2\right)\right]}\right)$$
(7)

The storage modulus and loss modulus in Equations (5) and (6), respectively, share identical model parameters because they derive from the same complex modulus. The loss factor is given by:

$$\tan \delta = \frac{\left(1 - G_g / G_e\right) \sin\left(\beta\theta\right)}{\left[1 + 2\omega^{\alpha} \tau^{\alpha} \cos\left(\alpha\beta/2\right) + \omega^{2\alpha} \tau^{2\alpha}\right]^{\beta/2} - \left(1 - G_g / G_e\right) \cos\left(\beta\theta\right)}$$
(8)

The relaxation time is the only temperature-dependent parameter in the Havriliak-Negami (HN) model. For multiple relaxations, more than one HN-equation is required [12]. To solve the HN model, the four temperature-independent parameters ( $G_g$ ,  $G_e$ , a,  $\beta$ ) are fitted in the complex plane of  $G^*$ , and the temperature-dependent relaxation time  $\tau$  (T) is directly calculated from the HN equation [13]. For the complex modulus determined at various temperatures and frequencies, the loss factor modulus points evaluated under these conditions could lie on a unique curve.

#### 2.2. Master Curves

Asphalt is considered a thermorheologically simple material in the Linear Viscoelastic (LVE) range, and the Time-Temperature Superposition Principle (TTSP) is applied to plot the master curves of various viscoelastic functions. The master curve is constructed as a function of the reduced frequency at an arbitrary reference temperature, as defined in the equation (9) [9]:

$$\rho_r = a_\tau \omega \tag{9}$$

where  $\omega_r$  is the reduced angular frequency, respectively;  $a_r$  is the time-temperature shift factor and changes with the temperature. The shift factor is obtained by the Williams-Landel-Ferry (WLF) equation, as follows:

$$\log_{10} a_{\tau} = -\frac{c_1 \left(T - T_0\right)}{c_2 + \left(T - T_0\right)} \tag{10}$$

where  $c_1$  and  $c_2$  are positive coefficients; T and  $T_0$  are test temperature and reference temperature, respectively.

The five HN model parameters ( $G_g$ ,  $G_e$ ,  $\alpha$ ,  $\beta$  and  $\tau_{\partial}$ ) and two parameters ( $c_1$  and  $c_2$ ) of the WLF equation are determined by applying a nonlinear minimization algorithm with the error function F estimated according to the Equation (11) [7]:

$$Error = Error_{G'} + Error_{G'}$$

$$F = \frac{1}{N} \sqrt{\sum_{j=1}^{N} \left(1 - \frac{G_{c}^{\prime j}}{G_{m}^{\prime j}}\right)^{2}} + \frac{1}{N} \sqrt{\sum_{j=1}^{N} \left(1 - \frac{G_{c}^{\prime \prime j}}{G_{m}^{\prime \prime j}}\right)^{2}}$$
(11)

where N is the number of the test data points for a single complex modulus component;  $G_c^{\prime j}$  and  $G_c^{\prime \prime j}$  are the storage and loss modulus derived from

Equations (5) and (6), respectively;  $G'_m{}^j$  and  $G''_m{}^j$  are the experimental storage and loss modulus, respectively. The error function was minimized through multiple iterations using the Solver function in Microsoft Excel [7] [14].

## 3. Experimental

#### 3.1. Materials

Asphalt AC-20 and styrene-butadiene-styrene (SBS) polymer were supplied by PEMEX (Salamanca, México) and Chemcentral, respectively. Nanoclay, surface-modified with 25 wt.% - 30 wt.% trimethyl stearyl ammonium, was supplied by Sigma-Aldrich, Mexico. The properties of neat asphalt and SBS polymer are shown in Table 1.

**Table 1.** Properties of asphalt AC-20; modifier polymer and Organic-Montmorillonite(OMMt) clay.

Material	Properties		
Asphalt	Penetration at 25°C; 67 dmm (ASTM D5) Softening point;		
	49°C (ASTM D36)		
	80% Maltenes and 20% asphaltenes (solubility in n-heptane		
	(ASTM standard D2042)		
Polymer	SBS Kraton D1102		
	30% wt.% of styrene		
	Linear		
	Mw: 71300 g/mol (GPC).		
Organic-Montmorillonite clay	Surface modified-contain 25 - 30 wt.% trimethyl stearyl		
	ammonium; density (Bulk density) 200 - 500 kg/m³		
(OMMt)	Average particle size $\leq 20$ $\mu$ m		

#### 3.2. Preparation of Modified Asphalt Binder

For the preparation of neat asphalt and asphalt blends (Asphalt/OMMt, Asphalt/SBS, and Asphalt/SBS/OMMt), a steel container was used at 180°C, stirring at 800 rpm under an inert atmosphere (N<sub>2</sub>). The mixing process continued for four hours to achieve uniform dispersion of clay. The concentration of SBS in asphalt was fitting at 4 wt.% for the samples asphalt/SBS (A/SBS), with 2.5 wt% of the Organic-Montmorillonite clay (OMMt) added to SBS and asphalt to produce A/OMMt, A/SBS, and A/SBS/OMMt blends. The samples were stabilized and stored in a freezer before further rheological testing.

#### 3.3. Conventional Test

The stiffness and high-temperature stability of the binders correlate with their penetration and softening point, respectively. The penetration test, conducted at 25°C with a 100 g load for 5 seconds, follows ASTM D5 guidelines. The softening point of asphalt was determined using the ring and ball test (ASTM-D36).

## 3.4. Rheological Analysis

The AR-1000-N rheometer was utilized for rheological testing in a controlled

stress mode, employing a parallel plate of 25 mm diameter and a 1.0 mm gap. The frequency range spanned from 0.1 to 100 rad/s, maintained at a constant temperature and strain. Tests were conducted at temperatures of 25, 40, 60, 75, and 100°C, ensuring the strain remained within the linear viscoelastic range [15].

## 4. Results and Discussion

**Figure 1** shows the penetration of asphalt blends decreases with the addition of SBS and clay, improving its consistency. The softening point rises with the addition of SBS or clay modifiers, thereby enhancing the asphalt binders rutting resistance.



**Figure 1.** Penetration (dmm) at 25°C and softening point (°C) of asphalt and blends.

**Figures 2(a)-(d)** display the curves of the dynamic mechanical moduli G' and G'' of asphalt and its blends or composites, measured across various constant temperatures as a function of frequency, along with the corresponding master curves. In **Figure 2(a)**, the moduli curves of G' and G'' of asphalt at a constant temperature show a gradual increase with the rising applied frequency. Similarly, the G' curves approach their corresponding G'' temperature-specific curves more closely, and their values rise as the measurement temperature decreases, leading to a crossover of G' and G'' at ~10<sup>2</sup> rad/s in the empirical-curves obtained at 25°C.

The master curve G' resembles an upward concave parabola at 100°C and quickly converges with the master curve G'' as the test temperature decreases until crossover. Concerning the rheological properties of asphalt, it is important to note that these properties are determined by the percentage of its components, typically classified into four categories based on their polarity: saturates, aromatics, resins, and asphaltenes. Resins and asphaltenes contribute to asphalt stiffness [16], while saturates and aromatics constitute the liquid phase. Thus, the crossover observed at ~25°C can be attributed to the  $T_g$  of resins, and the deviation in the moduli curves at 75°C may correspond to the cessation of Brownian motion in asphaltenes [17]. In turn, in **Figure 2(b)** (A/OMMt blend), curves of G' and G'' are similar in shape to those in Figure 2(a), but show an increase across the analyzed frequency range and exhibit a crossover at a frequency lower than  $10^2$  at 25°C. However, the onsets of G' and G'' are shifted to slightly higher values, possibly due to the interaction of asphalt with the OMMt particles, similar to what is observed in polymer composites containing OMMt particles [18]. This effect is attributed to interactions between components due to the quaternary ammonium salts in the OMMt clay, which likely facilitate the intercalation of asphalt molecules into the organo-clay layers. This process restricts the movement of asphalt molecule chains (possibly asphaltenes), as reported [19]. However, the interaction between asphalt and filler is complex, involving adsorption, diffusion, and infiltration of asphalt on the filler surface (asphalt-filler interface) [20]. The curves of A/OMMt, A/SBS, and A/SBS/OMMt blends, Figures 2(b)-(d), respectively, show the same trend of the Figure 2(a) but the crossover at 25°C shifted to low frequency in the order A/SBS/OMMt < A/SBS < A/OMMMt < A (Table 2). These results demonstrate how asphalt's interaction with OMMt and SBS, both separately and together, enhances its elastic properties, thereby increasing the glass transition temperature of maltenes and asphaltenes. This aligns with the reported compatibility of OMMt particles with both SBS and asphalt. The compatibility can be attributed to the hydrophobic nature of the Organic-Montmorillonite surface and the increased inter-layer distance, which facilitates the insertion of polymer chains and their intercalation into the clay layers, promoting the dispersion of clay within the polymer matrix [21].



**Figure 2.** Storage modulus and loss modulus master curves from HN model and experimental data: (a) Asphalt, (b) Asphalt/OMMt, (c) A/SBS, (d) A/SBS/OMMt.

The corresponding time-temperature shift factors ( $a_r$ ), measured at various temperatures at reference temperature ( $T_0 = 25^{\circ}$ C), are presented in **Figure 3**. The WLF constants,  $c_1$  and  $c_2$ , were approximately 4 and 312.5, respectively, similar to those reported elsewhere [14].



**Figure 3.** Time-temperature shift factors ( $a_{\tau}$ ) for asphalt and blends.

#### Havriliak-Negami Model

The master curves of dynamical moduli G' and G'' are used to assess structural changes through molecular mobility of the material. However, the correlation between the parameters of the HN model and molecular motions, polymer chain structure, and their interactions with asphalt and clay remains limited. The master curves of storage modulus and loss modulus (Figure 2) were determined using Equations (5) and (6) across various temperatures and frequencies for asphalt and blends. The optimized parameters for the HN model and WLF equation, along with the corresponding functional error values for all samples at a reference temperature of 25°C, were derived from Equations 9 - 11 and are displayed in Table 2. Model parameters for the samples at other temperatures were omitted due to space constraints. As mentioned above, G' and G'' increase with the addition of SBS and OMMt to the asphalt (Figure 2). The fit between the master curves from the experimental data and the HN model at 25 and  $40^{\circ}$ C is acceptable (error < 6 %). However, deviations were observed in the temperature range of 60°C - 75°C for the asphalt and blends, with errors ranging from 4.85% - 8.91%. This effect might be due to the contribution of the  $T_g$  of the asphaltenes, SBS and the deviation from the linear viscoelastic (LVE) region of the material [7]. Depending on the type of asphalt, it may present three main glass transition temperatures: one around -20°C, related to the maltene fraction,

Sample	$\omega_{\rm c}({\rm rad/s})$	G <sub>g</sub> (Pa)	Ge (Pa)	а	β	$ au_{ m HN}$	F (%)
Asphalt	79.43	$3.67 \times 10^{7}$	$1.46 \times 10^{-2}$	0.7017	0.1	$1.22 \times 10^{-2}$	2.03
A/OMMt	63.09	$4.58 \times 10^{7}$	$1.46 \times 10^{-2}$	0.6788	0.1	$1.15  imes 10^{-2}$	1.83
A/SBS	3.4	$6.84 \times 10^{7}$	$1.46  imes 10^{-2}$	0.5396	0.1	$1.36 \times 10^{-2}$	1.04
A/SBS/OMMt	$1.3\times10^{-2}$ and $5.32\times10^{-4}$	$8.76 \times 10^{7}$	$1.09 \times 10^{-9}$	0.5707	0.1	$3.35 \times 10^{-3}$	4.17

**Table 2.** Crossover, HN parameters at  $T_0 = 25^{\circ}$ C, and error, F.

followed by two endotherms at approximately 20°C and 50°C, corresponding to the melting of saturates. The other two  $T_g$ 's are 20°C for the resins and 53 to 70°C for asphaltenes [22]. Asphalt is generally a homogeneous mixture at temperatures above 70°C [23]. Therefore, the TTS principle may not apply across all temperature ranges due to changes in asphalt morphology. Furthermore, the yield stress fluid effect in neat asphalt (**Figure 2**) is temperature-dependent below 50°C and becomes somewhat independent at higher temperatures. This explains why the TTS cannot be strictly applied across all temperature ranges in asphalt, especially between 40°C - 75°C, where deviations from the master curves were observed in the HN model. Furthermore, the addition of clay increases the glass transition temperature of the base asphalt,  $T_{g, asphaltenes} \approx 50°C$ [24]. This effect is likely reflected in the increased error in the A/OMMt mixture within this temperature range (8.56% - 8.83 % error) (Figure 2(b)).

On the other hand, it has been reported that SBS exhibits two distinct glass transitions around  $-85^{\circ}$ C and  $95^{\circ}$ C, attributed to the polybutadiene (PB) and polystyrene (PS) blocks, respectively [25]. The triblock polymer prevents the dissolution of asphaltenes into maltenes, thereby favoring its preferential mixing with saturates and aromatic fractions, but not with asphaltenes. Consequently, the glass transition temperature ( $T_g$ ) of asphaltenes is influenced by SBS, shifting towards lower temperatures. This shift is particularly noticeable below  $68^{\circ}$ C, for example, with the transition at 40°C [26]. Regarding these facts, the mixing of asphalt primarily occurs with the PB midblock of SBS, altering its  $T_g$ , while the PS end blocks of the triblock polymer have a negligible effect on the asphalt's  $T_g$  [27]. This could explain the high error in the temperature range of 40°C - 75°C for A/SBS and A/SBS/OMMt samples. Furthermore, each experiment was repeated three times, with the mean error in the data observed to be within  $\pm 3.5\%$ , and the asphalt samples were in the LVE region.

The slopes of G'' at low and high frequencies are given by the *a*-parameter and  $\alpha\beta$ , respectively, according to Equation (12) [27]:

$$G'' \propto \omega^{\alpha}$$
 and  $G'' \propto \omega^{\alpha\beta}$  (12)

**Table 3** shows the slopes for all blends; the values of slope at low frequencies are in the range of 0.8416 - 0.9933, while at high frequencies the slope is lower (0.0842 - 0.09983).

Sample	Slope $G'' \approx \omega^{\alpha}$ ,	Slope $G'' \approx \omega^{\alpha\beta}$ ,
	low frequency	high frequency
Asphalt	0.9933	0.09983
A/OMMt	0.9923	0.09923
A/SBS	0.9459	0.09459
A/SBS/OMMt	0.8416	0.08416

**Table 3.** Effect of the  $\alpha$ - $\beta$  parameters in low and high frequencies.



**Figure 4.** *a*-parameter calculated with the HN model as a function of temperature for asphalt and its blends.

In addition, the prediction of G' and G'' are related to the rubbery regime at low-frequency  $G_e$  and the glassy regime modulus at high-frequency  $G_g$ . It depends on the properties of the volumetric fraction of components and the type of materials [7] For all samples,  $G_e$  values tend to be zero, indicating a trend toward a viscoelastic liquid at low-frequency and/or high-temperature conditions, while  $G_g$  is associated with physical hardening, with values higher at temperatures of 25°C.

On the other hand, it has been stated that the numerical values of the a and  $\beta$  parameters determine the relaxation mechanisms controlling the width and skewness of the loss peak, respectively [7]. These parameters are influenced by the similarities and differences in the types of inter- and intramolecular interactions present in the asphalt blends. Indeed, the parameter a can be correlated to the intermolecular dynamics, while the product  $a\beta$  corresponds to the local intramolecular dynamics of the polymer [28]. Despite the complexity of the asphalt blends analyzed in this study, it is possible to correlate experimental data with the dependence plot of a and  $\beta$  parameters based on their regularities. Figure 4 illustrates that the *a*-parameter rises with temperature and falls with the inclusion of SBS and OMMt in the blends. The *a*-values in the blends vary, suggesting they may be linked to the intermolecular interactions between the clay, polymer, and asphalt. Notably, the *a*-parameter of the A/OMMt blend is mar-

ginally lower than that of pure asphalt across the examined temperature range.

Furthermore, as reported in other studies [29], Organic-Montmorillonite can enhance the intercalation/exfoliation process, resulting in well-distributed clay particles within a hydrophobic asphalt. In the context of the A/SBS blend, the polymer may be absorbed by the maltenes, leading to polymer swelling and the formation of a polymeric network [30], but the low polarity of SBS results in weak interactions with asphalt. In the case of the A/SBS/OMMt blend, asphalt can swell the polymer and delaminate the clay, allowing polymer intercalation. However, moving the polymer within the clay interlayers is more challenging. The addition of clay enhances the physical and mechanical properties of the asphalt mixes, suggesting an increase in the rearrangement of the internal structure and in asphalt/polymer compatibility [29]. Thus, the addition of the SBS polymer, which is hydrophobic, and OMMt clay leads to physical interaction between the two components. This interaction improves the mechanical properties of the blends. Consequently, the  $\alpha$ -parameter of the A/SBS blend is slightly higher than that of the A/SBS/OMMt blend, and the *a*-parameter of both blends is lower than that of the neat asphalt, as observed in Figure 4. All analyzed samples showed a constant value of  $\beta \approx 0.1$  (Table 2). According to the literature, different values of the  $\beta$ -parameter were found for asphalt;  $\beta = 1.504 - 1.733$  in the HN model for three hot-mix asphalt mixtures (HMA) [14]. For two asphalt concrete mixtures at a reference temperature of 20°C, it was found that  $\beta = 0.327$ -0.368 [7], while for three asphalt mixtures,  $\beta = 0.13 - 5.44$  [5]. The HN model for asphalt concrete showed that  $\beta = 0.3163$  at a reference temperature of 0°C [30]. In addition, for six waste oils (WO) that modified asphalt at low temperature, it was found  $\beta = 14.935 - 16.499$  [6]. Nevertheless,  $\alpha$  and  $\beta$  parameters are taken as  $0 < \alpha < 1$ . When experiments conform to the HN model, they can exhibit typical ( $\beta \le 1$ ) or atypical relaxation behavior ( $\beta > 1$ ). If  $\beta > 1$ , it may indicate the superdiffusion movement of carriers and an inverse fractal dimension of the carrier paths [31].

The two relaxation processes depend differently on  $\tau$  in the temperature range analyzed. Thus, the relaxation process behavior of the asphalt corresponds to a distribution of relaxation times. These variations can be related to the motion or relaxation of asphalt, polymer, or clay particles, which are affected by temperature. For example,  $\tau_{HN}$  decreases, and hence, the molecular mobility increases. Thus, relaxation spectra can aid in the physical interpretation of the structural and mechanical properties of asphalt mixtures [7]. The relaxation time ( $\tau_{HN}$ ) for all samples is shown in **Figure 5**. The  $\tau_{HN}$  increases in the blends and decreases in the asphalt (**Table 2**). However, the potential error in the calculated relaxation time values within the temperature range of 60°C -75°C must be taken into account. As previously mentioned, SBS and OMMT likely exhibit distinct intra- and inter-molecular interactions with asphalt. Yet, a precise physical interpretation of relaxation time in asphalt blends remains uncertain, as discussed earlier. The master curves of complex modulus ( $G^*$ ) versus reduced frequency ( $\omega^*$   $a_r$ ) for asphalt and blends are depicted in **Figure 6**. As anticipated, the  $G^*$  values are higher in the blends than in the neat asphalt. However, the loss factor (*tan*  $\delta$ ) exhibited deviations in the superposition of the experimental data (**Figures 7(a)-(b**)), particularly at low frequencies, with the lowest values corresponding to the A/SBS and A/SBS/OMMt blends.



**Figure 5.** Relaxation time ( $\tau_{HN}$ ) with the temperature for the different samples estimated with HN model.



**Figure 6.** Master curves of the complex moduli  $(G^*)$  for all blends.



**Figure 7.** The loss factor (tan  $\delta$ ) at different temperatures for (a) Asphalt and A/OMMt; b) A/SBS, and A/SBS/OMMt.

These plots revealed that OMMt significantly increases asphalt stiffness at low frequencies (or high temperatures). However, at high frequencies, the master curves for different blends are similar, indicating that clay's impact on asphalt stiffness is negligible.

Finally, the Black diagram, shown in **Figure 8**, demonstrates that none of the three asphalt blends adhere to the time-temperature superposition principle, resulting in non-unique curves. For such complex materials, the fundamental assumption of time-temperature equivalence leads to prediction errors. The binders start to deviate from thermorheological simplicity as the phase angle nears 90°C at high temperatures, where some experimental points do not align with the rest. These materials exhibit only partial thermorheological simplicity.

The high viscosity of asphalt binders, as shown in **Figure 9**, results from adding solid particles to the asphalt matrix, affecting the Newtonian plateau at low frequencies in the case of A/SBS/OMMt. Following the Newtonian plateau, a transition zone with decreased viscosity at intermediate and high frequencies is observed. The viscosity enhancement in asphalt blends depends on the interactions among blend components. For example, A/SBS and A/SBS/OMMt form a polymer network, while the clay changes the effective volume fraction, interfacial tension, and increases the tendency to attract surrounding chemical species. The filler effect is attributed to reduced polymer chain mobility and increased flow resistance in the asphalt blend. This suggests that clay particles could serve as a compatibility activator by facilitating the transfer of maltenes and highly polar fractions from the asphaltene-rich phase to the polymer-rich phase [19].



Figure 8. Black diagram for neat asphalt and blends.



Figure 9. Master curve of complex viscosity of neat asphalt and blends.

## **5.** Conclusion

The master curves of the viscoelastic function were obtained using the shift factor calculated for each temperature. The experimental data for asphalt and its blends were simultaneously adjusted to the HN model, which accurately predicts the G', G'' and the complex modulus for asphalt and composites at low temperatures (25°C - 40°C). Whereas in the range of temperatures of 40°C - 75°C, the prediction of G' and G'' modulus exhibited high errors (approx. 5% -9%) because this range includes the  $T_g$  of asphalt and the polymer SBS, rendering the HN model ineffective for the systems studied under these conditions. However, at 100°C, the prediction error of the HN model was reduced to 2.3% -2.8% for asphalt and its mixtures, demonstrating a viscous rubber-like behavior. The  $\alpha$ -parameter of the HN model increases with temperature and decreases with the addition of OMMt and SBS, while the  $\beta$ -parameter remains practically constant. Relaxation time ( $\tau_{HN}$ ) increases with both temperature and the addition of asphalt modifiers, leading to reduced molecular mobility. This study concludes that asphalt and its blends are thermorheologically complex, and the applicability of the viscoelastic HN model is limited due to interactions among asphalt components and modifiers. These interactions, potentially influenced by the glass transition temperatures of SBS and asphalt, significantly alter the rheological properties of asphalt and its blends. Predicting the dynamic viscoelastic properties of asphalt binders at different frequencies (temperatures) using the HN model is insufficient if the temperature range includes the  $T_g$  of one or more components. As a result, the correlation between the structure and mechanical properties of asphalt blends and the parameters of the HN model is not sufficiently strong.

# Acknowledgments

The authors gratefully acknowledge the financial support to Technological National of México, Project number (5503.19-P).

# **Author Contributions**

María de los Ángeles Vargas Hernández: Funding acquisition (supporting), visualization, investigation, original draft preparation. Miguel Ángel Vargas: supervision, software. Pedro Raymundo García Morán: parameter fitting and edition text. Humberto Vázquez Torres: reviewing, editing, supervision.

# **Data Availability Statement**

The experimental data that support this work are available from the corresponding author upon reasonable request.

# **Conflicts of Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# References

- [1] Piskunov, I.V., Bashkirceva, N.Y. and Emelyanycheva, E.A. (2022) The Mathematical Modeling of Bitumen Properties Interrelations. *Journal of Chemical Technology and Metallurgy*, **57**, 464-479.
- [2] Wang, H., Guo, Y., Shen, A., Yang, X. and Li, P. (2020) Effect of Nanoclays on Moisture Susceptibility of SBS-Modified Asphalt Binder. *Advances in Materials Science and Engineering*, 2020, Article 2074232. <u>https://doi.org/10.1155/2020/2074232</u>
- Yılmaz, B. and Ebru Gürbüz, H. (2021) Rheological and Morphological Evaluation of Nanoclay Modified Asphalt Binder. *Construction and Building Materials*, **313**, Article 125479. <u>https://doi.org/10.1016/j.conbuildmat.2021.125479</u>
- [4] Yadykova, A.Y. and Ilyin, S.O. (2023) Bitumen Improvement with Bio-Oil and Natural or Organomodified Montmorillonite: Structure, Rheology, and Adhesion of Composite Asphalt Binders. *Construction and Building Materials*, 364, Article 129919. <u>https://doi.org/10.1016/j.conbuildmat.2022.129919</u>
- [5] Yu, D., Yu, X. and Gu, Y. (2020) Establishment of Linkages between Empirical and Mechanical Models for Asphalt Mixtures through Relaxation Spectra Determination. *Construction and Building Materials*, 242, Article 118095. <u>https://doi.org/10.1016/j.conbuildmat.2020.118095</u>
- [6] Xu, J., Fan, Z., Lin, J., Yang, X., Wang, D. and Oeser, M. (2021) Predicting the Low-Temperature Performance of Asphalt Binder Based on Rheological Model. *Construction and Building Materials*, **302**, Article 124401. https://doi.org/10.1016/j.conbuildmat.2021.124401
- [7] Sun, Y., Chen, J. and Huang, B. (2015) Characterization of Asphalt Concrete Linear Viscoelastic Behavior Utilizing Havriliak-Negami Complex Modulus Model. *Construction and Building Materials*, **99**, 226-234. <u>https://doi.org/10.1016/j.conbuildmat.2015.09.016</u>

- [8] Hernandez-Fernandez, N. and Ossa-Lopez, A. (2021) Validation of Partial Time-Temperature Superposition Principle in Thermorheologically Complex Asphalts. *Construction and Building Materials*, 276, Article 122224. <u>https://doi.org/10.1016/j.conbuildmat.2020.122224</u>
- [9] Huang, Y., Hou, H., Oterkus, S., Wei, Z. and Zhang, S. (2018) Mechanical and Acoustic Performance Prediction Model for Elastomers in Different Environmental Conditions. *The Journal of the Acoustical Society of America*, 144, 2269-2280. https://doi.org/10.1121/1.5063355
- [10] Liu, N., Chen, Y., Zhou, J. and Huang, Y. (2023) Superconvergence Analysis for Time-Domain Maxwell's Equations in a Havriliak-Negami Dispersive Medium. *Applied Mathematics Letters*, 145, Article 108762. <u>https://doi.org/10.1016/j.aml.2023.108762</u>
- [11] Hartmann, B., Lee, G.F. and Lee, J.D. (1994) Loss Factor Height and Width Limits for Polymer Relaxations. *The Journal of the Acoustical Society of America*, **95**, 226-233. <u>https://doi.org/10.1121/1.408355</u>
- [12] Madigosky, W.M., Lee, G.F. and Niemiec, J.M. (2006) A Method for Modeling Polymer Viscoelastic Data and the Temperature Shift Function. *The Journal of the Acoustical Society of America*, **119**, 3760-3765. <u>https://doi.org/10.1121/1.2195292</u>
- Szabo, J.P. and Keough, I.A. (2002) Method for Analysis of Dynamic Mechanical Thermal Analysis Data Using the Havriliak-Negami Model. *Thermochimica Acta*, 392, 1-12. <u>https://doi.org/10.1016/s0040-6031(02)00064-3</u>
- [14] Wang, Y., Zhao, Y., Sun, Q. and Fu, G. (2023) Influence of Bedrock on Viscoelastic Responses and Parametric Back-Calculation Results for Asphalt Pavements and Prediction of Bedrock Depth under FWD Tests. *Construction and Building Materials*, **377**, Article 131158. <u>https://doi.org/10.1016/j.conbuildmat.2023.131158</u>
- [15] Vargas-Hernández, M.A. and Vazquez-Torres, H. (2015) Rheological Characterization and Thermal Stability of Triblock Copolymers-Modified Asphalt Reinforced with Mont-Morillonite Nanoparticles in Physical Mixing. *Revista Mexicana de Ingeniería Química*, 14, 503-512.
- [16] Salehfard, R., Behbahani, H., Dalmazzo, D. and Santagata, E. (2021) Effect of Colloidal Instability on the Rheological and Fatigue Properties of Asphalt Binders. *Construction and Building Materials*, 281, Article 122563. <u>https://doi.org/10.1016/j.conbuildmat.2021.122563</u>
- [17] Porto, M., Angelico, R., Caputo, P., Abe, A.A., Teltayev, B. and Rossi, C.O. (2022) The Structure of Bitumen: Conceptual Models and Experimental Evidences. *Materials*, **15**, Article 905. <u>https://doi.org/10.3390/ma15030905</u>
- [18] Wu, W., Jiang, W., Yuan, D., Lu, R., Shan, J., Xiao, J., et al. (2021) A Review of Asphalt-Filler Interaction: Mechanisms, Evaluation Methods, and Influencing Factors. Construction and Building Materials, 299, Article 124279. https://doi.org/10.1016/j.conbuildmat.2021.124279
- [19] Zhang, H., Zhang, D. and Zhu, C. (2015) Properties of Bitumen Containing Various Amounts of Organic Montmorillonite. *Journal of Materials in Civil Engineering*, 27. <u>https://doi.org/10.1061/(asce)mt.1943-5533.0001261</u>
- [20] Debbarma, K., Debnath, B. and Sarkar, P.P. (2022) A Comprehensive Review on the Usage of Nanomaterials in Asphalt Mixes. *Construction and Building Materials*, 361, Article 129634. <u>https://doi.org/10.1016/j.conbuildmat.2022.129634</u>
- [21] Tang, N., Yang, J., Cen, W., Pan, W., Wu, L. and Xu, C. (2021) Preparation of Organic Montmorillonite Promoter for Improving the Adhesion between Bitumen and Acidic Aggregate. *Construction and Building Materials*, 274, Article 121833.

https://doi.org/10.1016/j.conbuildmat.2020.121833

- Mouazen, M., Poulesquen, A. and Vergnes, B. (2011) Correlation between Thermal and Rheological Studies to Characterize the Behavior of Bitumen. *Rheologica Acta*, 50, 169-178. <u>https://doi.org/10.1007/s00397-011-0534-5</u>
- [23] Merusi, F., Polacco, G., Filippi, S. and Giuliani, F. (2013) Structural Transitions and Physical Networks in Wax-Modified Bitumens. *Road Materials and Pavement Design*, 14, 289-309. <u>https://doi.org/10.1080/14680629.2013.792292</u>
- [24] Kumar, Y., Singh, S.K., Oberoi, D., Kumar, P., Mohanty, P. and Ravindranath, S.S. (2020) Effect of Molecular Structure and Concentration of Styrene-Butadiene Polymer on Upper Service Temperature Rheological Properties of Modified Binders. *Construction and Building Materials*, 249, Article 118790. https://doi.org/10.1016/j.conbuildmat.2020.118790
- [25] Rasool, R.t., Song, P. and Wang, S. (2018) Thermal Analysis on the Interactions among Asphalt Modified with SBS and Different Degraded Tire Rubber. *Construction and Building Materials*, **182**, 134-143. https://doi.org/10.1016/j.conbuildmat.2018.06.104
- [26] Laukkanen, O., Soenen, H., Winter, H.H. and Seppälä, J. (2018) Low-Temperature Rheological and Morphological Characterization of SBS Modified Bitumen. *Construction and Building Materials*, **179**, 348-359. https://doi.org/10.1016/j.conbuildmat.2018.05.160
- [27] Masson, J., Polomark, G. and Collins, P. (2005) Glass Transitions and Amorphous Phases in SBS-Bitumen Blends. *Thermochimica Acta*, **436**, 96-100. <u>https://doi.org/10.1016/j.tca.2005.02.017</u>
- [28] Liau, W.B. (1999) Dynamic Mechanical Relaxation of Lightly Cross-Linked Epoxidized Natural Rubber. *Polymer*, 40, 599-605. <u>https://doi.org/10.1016/s0032-3861(98)00286-9</u>
- [29] Mortezaei, M., Shabani, S. and Mohammadian-Gerzaz, S. (2020) Assessing the Effects of Premixing on the Rheological Properties for Three-Phases Asphalt Binder Nano-Composite Including Clay and SBS. *Construction and Building Materials*, 231, 117151. <u>https://doi.org/10.1016/j.conbuildmat.2019.117151</u>
- [30] Gudmarsson, A., Ryden, N. and Birgisson, B. (2012) Characterizing the Low Strain Complex Modulus of Asphalt Concrete Specimens through Optimization of Frequency Response Functions. *The Journal of the Acoustical Society of America*, 132, 2304-2312. <u>https://doi.org/10.1121/1.4747016</u>
- [31] Khamzin, A.A. (2019) Trap-Controlled Fractal Diffusion Model of the Havriliak-Negami Dielectric Relaxation. *Journal of Non-Crystalline Solids*, **524**, Article 119636. <u>https://doi.org/10.1016/j.inoncrysol.2019.119636</u>