CHAPTER 4
Development of Mathematical Models for Frequency Dependency

4.1. INTRODUCTION

Asphalt paving technologists have described the rheological and chemical changes associated with laboratory short term and long term aging of unmodified base asphalt. However, although the rheological and chemical interaction between the asphalt and polymer has been investigated, it has not been quantified. A general model that can predict the viscoelastic behavior of polymer-modified binder is needed to describe their rheological response. Asphalt binders experience three regions of behavior (Marasteanu *et al.*, 1996):

1. Non-equilibrium behavior at temperatures below the glass transition temperature.
2. Thermal-rheologically simple linear viscoelastic behavior in the temperature range between the glass transition temperature (T_g) and T_g + 100°C.
3. Newtonian behavior at elevated temperatures, typically at temperatures greater than T_g + 100°C.

The objective of this study was to develop a mathematical model to accurately describe modified and straight binder behavior in the thermal-rheological simple linear viscoelastic region. As presented in Chapter 2, various models have been introduced to fulfill this goal since the early fifties. Most of these models were found to suffer at least one of the following drawbacks:

- Excessive complexity to be used in practice (e.g. Jongepier and Kuilman's model, Dickinson and Witt's model, Stastna and Zanzotto's model).
- Lack of theoretical rigorousness (e.g. Gahvari's model, statistical models).
- Lack of generality required to model modified binders. Most of the available models were developed based only on straight binder experimental data and did not accurately fit modified binders (e.g. Christensen and Anderson's models, Dobson's model).

Before addressing the derivation of the models, a description of the problem is presented to identify the key variables in the system.

4.2. SYSTEM MODELING

A model is defined as an abstraction of reality that captures the functional essence of the system to be used instead of the system for investigation and experimentation which involves less risk, less time, and less money (Trani, 1999). From the previous definition, one can state that the purposes of a model are as follows:

- To predict system behavior
- To learn by experience
- To communicate system behaviors to others
- To plan strategies to control system behavior

To develop a model, several steps need to be followed. These steps, presented in Figure 4.1, can be summarized as follows:

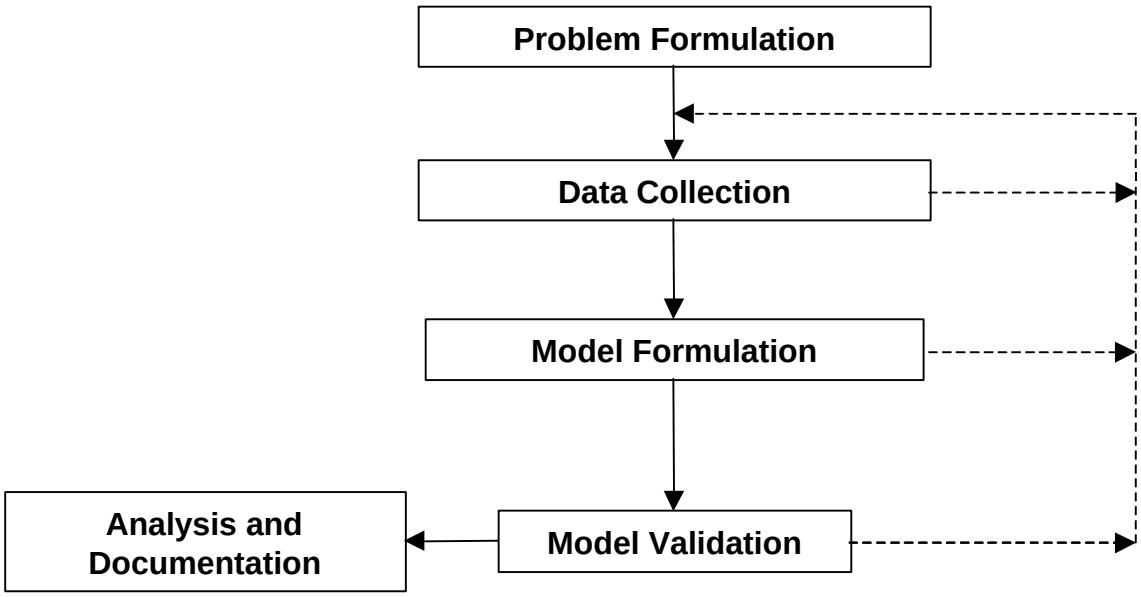

Figure 4.1. The Modeling Process (after Trani, 1999)

- Verbal description of the problem (Problem Formulation)
- Data Collection
- Construction of the mathematical model (Model Formulation)
- Validation of the model
- Analysis of the model
- Monitoring the system so as to calibrate and update the model (Documentation)

Before developing a model, it is important to construct a causal diagram, which identifies the key variables in the system. The causal diagram representing our system is illustrated in Figure 4.2. As can be seen in the causal diagram, two main factors are controlling the rheological behavior of asphalt binders: loading time and temperature. The traditional approach to dealing with this system is to reduce the three dimensional problem to a two dimensional problem by using the Time Temperature Superposition Principle (see Chapter 2). The loading amplitude is dealt with by considering the behavior within the region of linear response. Although more sophisticated non-linear models are available, such models are mathematically complicated and extensive testing is required to fully describe the parameters that describe these models (Bernstein, 1963).

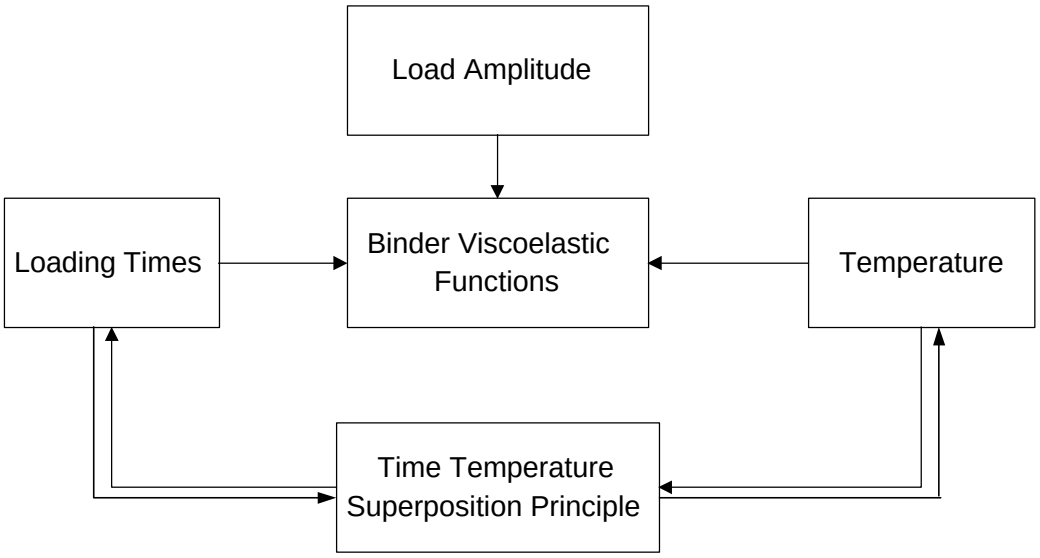

Figure 4.2. Causal Diagram for the Binder Viscoelastic System

By considering the previous assumptions, the system can be modeled with only one control variable: loading time or frequency.

4.3. DEVELOPMENT OF A MATHEMATICAL MODEL FOR THE COMPLEX SHEAR MODULUS

This section introduces the representation of linear viscoelastic behavior by mathematical models that bear no relationship to the superposition principle. These models are useful when it is desired to describe linear viscoelastic behavior by a small, easily manageable, number of parameters. Being essentially empirical curve-fitting equations containing adjustable parameters, these mathematical models are more flexible than other models (e.g. ladder models). However, they suffer from the disadvantage that if one of these mathematical models adequately describes the response of a linear viscoelastic material to a given excitation, it is not possible to convert this model to describe another type of excitation. In applications in which interconvertibility is not an issue, the simplicity of the mathematical models overcomes their lack of a proper foundation in the theory of linear viscoelastic behavior. One way of deriving such models is the matching function approach that will be used in this study. This method was introduced by Nicholas W. Tschoegl (1918-) in his book The Phenomenological Theory of Linear Viscoelastic Behavior: An Introduction.

For the case of a harmonic response function, it was shown in Chapter 2 that the complex shear modulus (G*) can be written as follows (Equation 2.26):

$$G^*(w) = G_e + \int_{-\infty}^{\infty} H(t) \frac{jwt}{1+jwt} d\ln t \qquad (4.1)$$

where,

$G^*(\omega)$ is the complex shear modulus at frequency ω;

G_e is the equilibrium shear modulus;

$H(\tau)$ is the relaxation spectrum; and

τ is the relaxation time.

To facilitate the discussion, a dimensionless response function that has the same general features as the corresponding kernel function is introduced. The dimensionless functions are obtained using Equation 4.1:

$$Z_H(w) = \frac{\int_{-\infty}^{\infty} H(t)\,k(w,t)\,d\ln t}{\int_{-\infty}^{\infty} H(t)\,d\ln t} \tag{4.2}$$

where $k(\omega,\tau)$ is the kernel function. Equation 2.25 can be written as follows:

$$\overline{Q}(s) = G_e + \int_{-\infty}^{\infty} H(t)\,k(s,t)\,d\ln t \tag{4.3}$$

from which one obtains the following:

$$G_e - \overline{Q}(s) = -\int_{-\infty}^{\infty} H(t)\,k(w,t)\,d\ln t \tag{4.4}$$

where G_e is the equilibrium shear modulus. Recalling Equation 2.29:

$$G_g - G_e = \int_{-\infty}^{\infty} H(t)\,d\ln t \tag{4.5}$$

Substituting Equations 4.5 and 4.4 into 4.2 results in the following:

$$\overline{Q}(s) = G_g - [G_g - G_e]\,Z_H(w) \tag{4.6}$$

Just as the respective kernel functions, the functions $Z_H(\omega)$ are characterized by the relation $1 \geq Z_H(\omega) \geq 0$. These functions should be monotone non-increasing function of their arguments. Direct assumption of the $Z_H(\omega)$ operator allows modeling the respondances $\overline{Q}(s)$ from which any standard response function can be obtained

according to Table 2.2. At the limits of their domain, a suitable Z function should satisfy the following two limits:

$$\lim_{x\to 0} Z(x) = 1 \qquad \text{and} \qquad \lim_{x\to \infty} Z(x) = 0 \qquad (4.7)$$

The model development is thus reduced to select a mathematical function Z(ω) that fulfills the previous set of conditions and *matches* the viscoelastic function of interest (i.e. G*(ω)). A suitable Z function contains at least two parameters, one for locating it along the time or frequency axis, and another to regulate its spread. Clearly, a large number of functions that respect the previous conditions can be found. Table 4.1 presents some famous forms introduced in different fields of science. In this table, the parameter that determines the location of the function along the log x-axis is denoted by the same symbol, x_0, in all cases. The other parameters in each model govern the spread of the function along the x-axis (k, c, p, b, and v).

Table 4.1. Matching Functions of the Z-type

Function Name	Form	Field introduced
Kohlrausch (1863)	$Z(x) = \exp[-(x/x_0)^k]$	Torsion of Glass Fibers
Cole-Cole (1941)	$Z(x) = \frac{1}{1+(x/x_0)^c}$	Complex Dielectric Constant
Hyperbolic Tangent Function	$Z(x) = \tanh(x_0/x)^p$	Ladder Modeling
Kobeko Function (1937)	$Z(x) = \frac{1}{(1+x_0/x)^b}$	Dielectric Constant
Havriliak and Negami (1966)	$Z(x) = \frac{1}{[1+(x/x_0)^v]^w}$	Dielectric Constant

It can be noticed that some of these functions are derived from the kernel functions of the canonical representation of some of the viscoelastic functions (e.g. Cole-Cole function). One function of particular interest in the rest of the formulation is the Havriliak and Negami model presented in Table 4.1. This model contains both the Cole-Cole and

the Kobeko models as special cases when w=1, v = c, and w = b, v = 1, respectively. Figure 4.2 presents the behavior of this function over a wide range of frequency (ω). It can be seen that this function satisfies the conditions previously stated:

- $\lim_{w \to 0} Z(x) = 1$
- $\lim_{w \to \infty} Z(x) = 0$
- Z(x) possesses three parameters with x_0 (or ω_0) responsible for the location of the function along the x-axis.

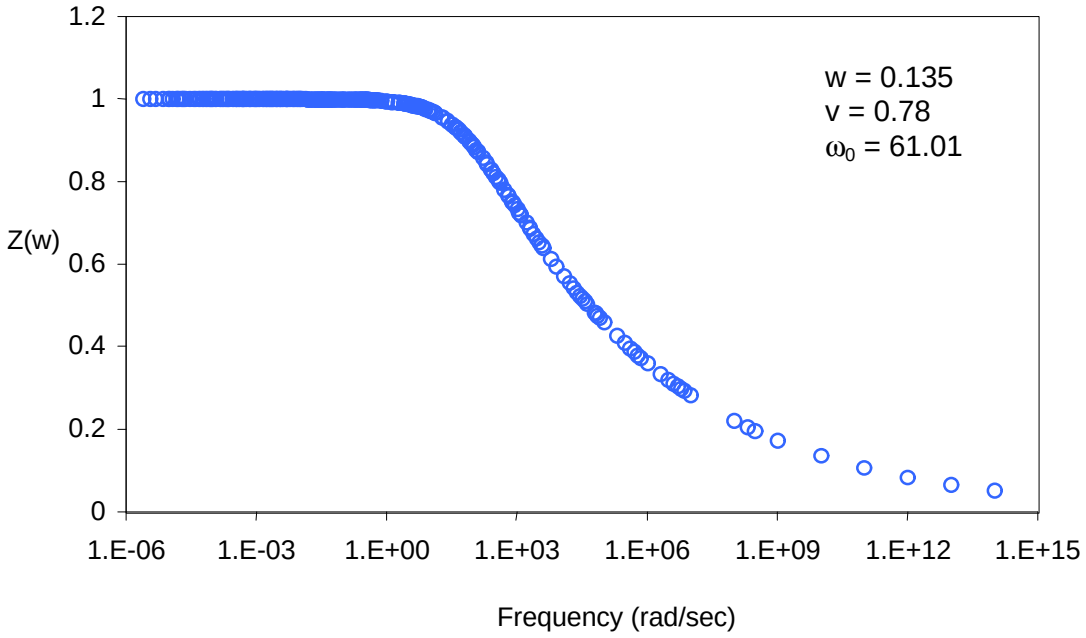

Figure 4.3. The Havriliak and Negami Model

It has been shown in Table 2.2 that the complex shear modulus (G*(ω)) can be obtained from the retardance ($\overline{Q}(s)$) as follows:

$$G^*(\omega) = \overline{Q}(s)\big|_{s=jw} = \overline{Q}(jw) \qquad (4.8)$$

From Equation 4.6 and 4.8, we obtain:

$$G^*(w) = G_g - [G_g - G_e]\ Z(jw) \tag{4.9}$$

Since asphalt binder is a rheodictic material, G_e=0, from which Equation 4.9 becomes:

$$G^*(w) = G_g[1 - Z(jw)] \tag{4.10}$$

Recalling the Havriliak-Negami model in its general form:

$$Z_v^*(w) = \frac{1}{[1 + (jw/w_o)^v]^w} \tag{4.11}$$

where,

$Z_v^*(w)$ is a dimensionless complex function that takes a value between zero and one;

ω is the reduced frequency;

v and w are model parameters; and

ω_o is a reduced frequency value that defines the location along the x-axis.

Separating the real and imaginary parts leads to:

$$Z_v'(w) = \frac{(w_o/w)^{vw/2}\cos wf(w)}{[(w_o/w)^v + 2\cos vp/2 + (w/w_o)^v]^{w/2}} \tag{4.12}$$

and

$$Z_v''(w) = \frac{(w_o/w)^{vw/2}\sin wf(w)}{[(w_o/w)^v + 2\cos vp/2 + (w/w_o)^v]^{w/2}} \tag{4.13}$$

with

$$\tan f(w) = \frac{\sin vp/2}{(w_o/w)^v + \cos vp/2} \tag{4.14}$$

For the Havriliak-Negami form, it might be shown using Equation 4.10 that the complex modulus components are obtained by the following:

$$G_c^{'}(w) = G_g[1 - \frac{(w_o/w)^{vw/2}\cos(w\tan^{-1}f(w))}{[(w_o/w)^v + 2\cos pv/2 + (w/w_o)^v]^{vw/2}}] \quad (4.15)$$

and

$$G_c^{''}(w) = G_g \frac{(w_o/w)^{vw/2}\sin(w\tan^{-1}f(w))}{[(w_o/w)^v + 2\cos pv/2 + (w/w_o)^v]^{vw/2}} \quad (4.16)$$

where,

v and w are the model parameters (0-1);

ω_o is a location frequency (rad/sec); and

G_g is the glassy shear modulus (Pa).

Unfortunately, the functions resulting from separating the real and imaginary parts of the formulated retardance $\overline{Q}(s)$ are not quite practical due to the mathematical complexity of the Equations. Moreover, the models do not fit the experimental results (Figure 4.4). As presented in this figure, it seems impossible to reach an acceptable convergence between the two sets; thus, a new approach needs to be developed.

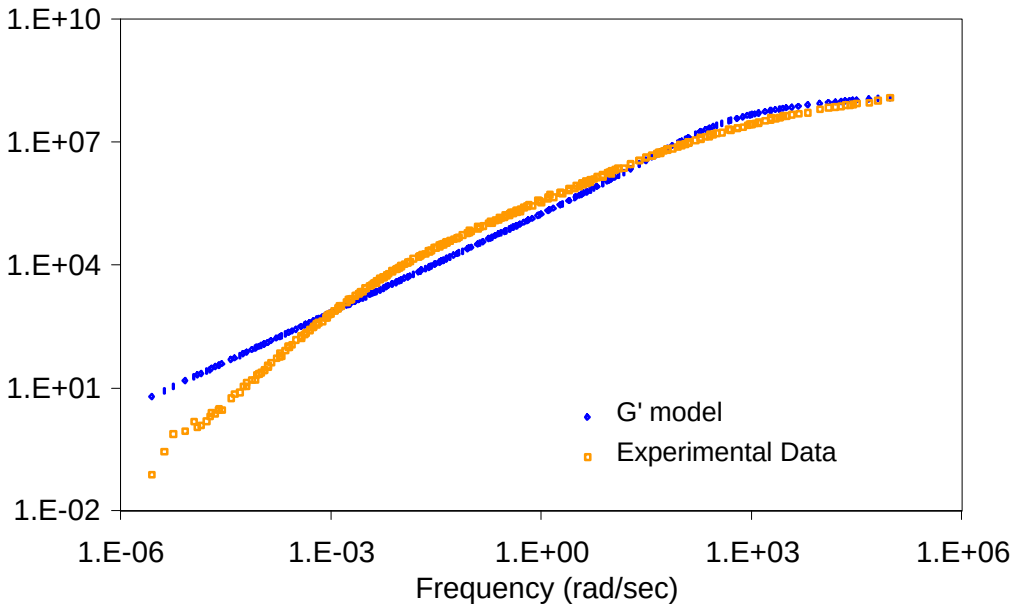

Figure 4.4. Poor Matching of the First Proposed Model

Consequently, assuming that |G*| is a response function that can be formulated similarly, results in the following equation by omitting the complex factor, j, from Equation 4.11:

$$Z_v^*(w) = \frac{1}{[1+(w/w_o)^v]^w} \tag{4.17}$$

The only shortcoming of this assumption is that the generated G* function will not be self-consistent with the other response functions. However, as asphalt rheologists are interested mainly in the complex shear modulus, this is not a serious drawback. It should be noted that modeling of the complex shear modulus absolute value was also followed in the SHRP procedure (Christensen *et al.*, 1992). Directly modeling the complex shear modulus does not affect the main assumptions in the formulation of a theoretical model as long as the rules for the Z(ω) dimensionless function are respected. Using Equation 4.17, the resulting model takes the following form:

$$|G^*(w)| = G_g[1 - \frac{1}{[1+(w/w_o)^v]^w}] \tag{4.18}$$

The parameters of this model are as follows:

- v (0-1) that controls the rotation of the model (Dimensionless).
- ω_0 that defines the location along the x-axis with unity of frequency (r/s).
- w (greater than zero) that defines the location along the y-axis (Dimensionless).

Other Z functions were tested (e.g. Cole-Cole function, Kobeko function), but the Negami function showed the best fit. In order to judge the accuracy of this model, the results were compared to the dynamic master curves showing an acceptable fit that will be evaluated on the following chapter. Figure 4.5 presents the comparison for the PG 76-22P binder. The parameters of the model were obtained using non-linear regression, which will be elaborated later in this chapter.

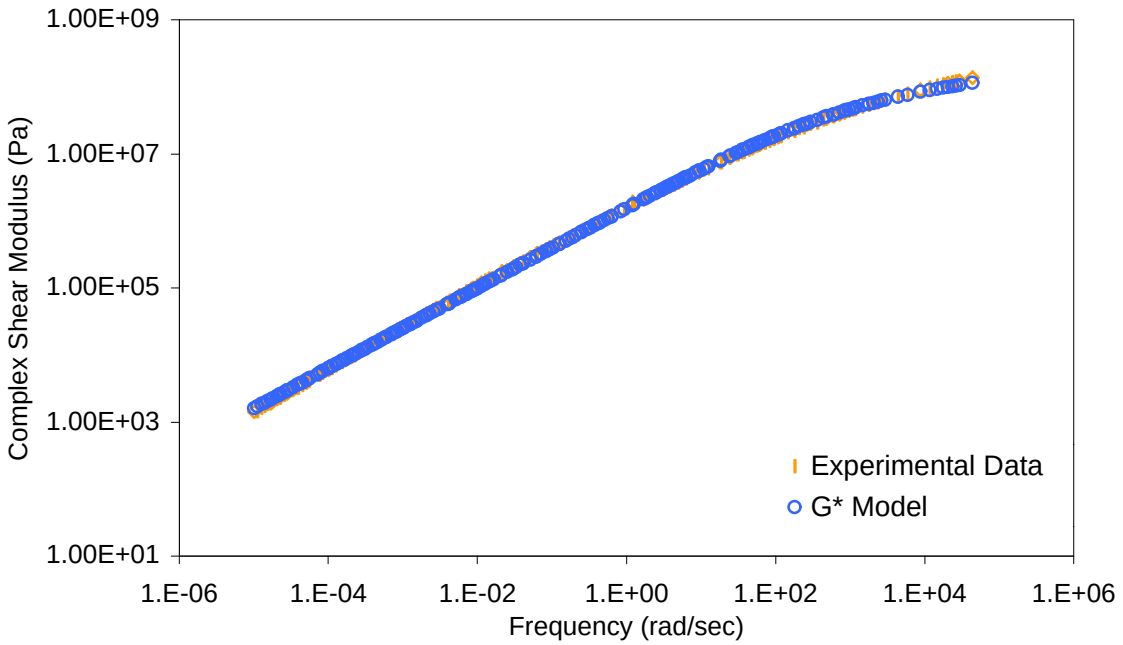

Figure 4.5. Comparison between the Measured Complex Shear Modulus for PG 76-22P and Results of the Proposed Model

4.4. DEVELOPMENT OF A MATHEMATICAL MODEL FOR THE PHASE ANGLE

As explained in Chapter 2, most of the models that describe the frequency dependency of asphalt binder rely on some approximate interrelationship between viscoelastic functions. One of these relations is the Booij and Thoone (1982) approximation that assumed that the Kramers-Kronig relations might be written as follows:

$$d(w) \cong \frac{p}{2}\left(\frac{d\ln|G^*(w)|}{d\ln w}\right) \tag{4.19}$$

The Kramers-Kronig relations indicate that the frequency dependencies of the real and the imaginary parts of a system function are not independent from each other. They also imply that the absolute value and the argument of the system function should be interrelated.

As noticed, this relation suggests that the phase angle is the slope of the complex shear modulus on a log-log plot. Although Booij and Thoone (1982) supported the accuracy of this relation for describing the rheological properties of different classes of polymers, analyses of the dynamic data for asphalt binder show that this relation does not hold true for asphalt binder. According to Booij (1982), this relation is only valid for viscoelastic solid:

$$\lim_{w \to 0} G^*(iw) = 0 \tag{4.20}$$

For viscoelastic liquids such as asphalt binder (Dickinson *et al.*, 1974), the following equation is valid:

$$\lim_{w \to 0} \frac{G^*(iw)}{iw} = h(0) \tag{4.21}$$

where $\eta(0)$ is the Newtonian viscosity at very low frequencies.

Therefore, for asphalt binder the quantity $G^*(i\omega)$ does not meet the requirements for the Kramers-Kronig relations. The mathematical Equations for the phase angle in both Dickinson and Witt's (1974) and Christensen and Anderson's (1992) models were derived based on this approximation.

The formulation of the phase angle also uses the previously introduced $Z(\omega)$ function ranging between zero and unity known as the Havriliak and Negami model. If this function is multiplied by a scaling factor, 90 degrees, the resulting model ranges between zero and 90°, which is the range for the phase angle. The resulting model has the following form:

$$d(\text{degrees}) = \frac{90}{\left[1 + (w / w_0)^{v}\right]^{w}} \tag{4.22}$$

An example of the fit of this model to actual experimental data is presented in Figure 4.6 for the PG 64-22 unaged binder. It must be noticed that the parameters ω_0, v, and w are determined statistically and have different values in the |G*| and δ models.

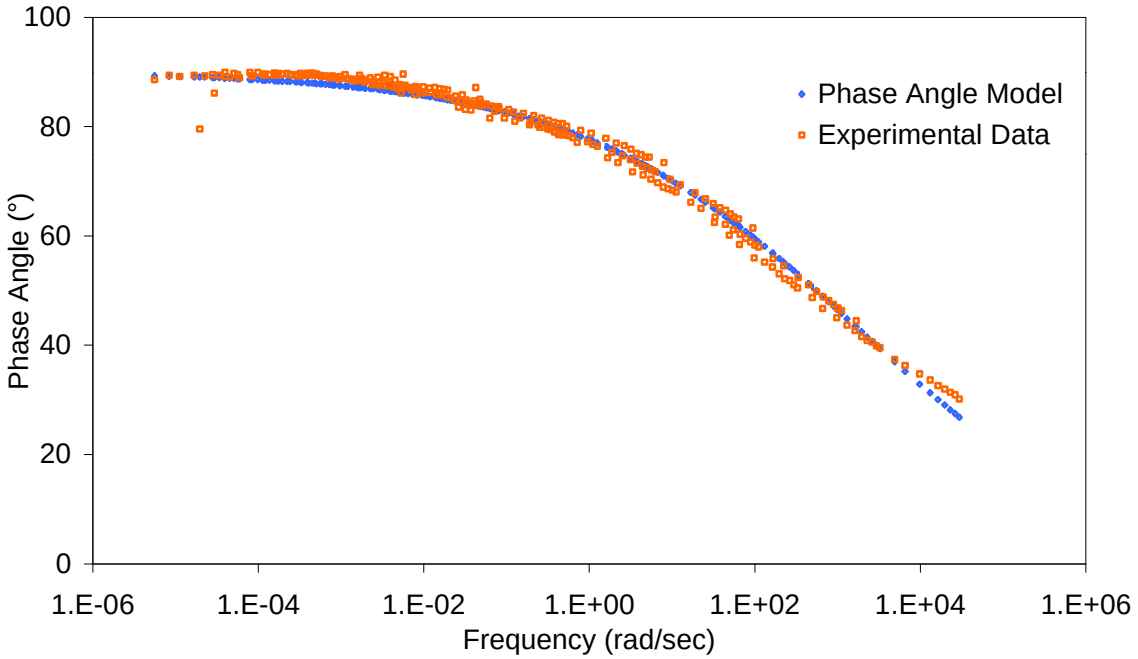

Figure 4.6. Comparison between the Measured Phase Angle for PG 64-22U and the Proposed Model

An interesting feature of polymer-modified binders is the presence of a small plateau region in the phase angle master curves. This region was not noticed in unmodified binders (see Figure 4.6) and may be attributed to the formation of a polymeric network within the binder (Gahvari, 1996). The proposed model could not simulate this region very accurately. However, the difference between the model prediction and the experimental results was less than 10% of the exact value, which is within the ranges of the expected experimental errors in such tests. The model validation is elaborated in detail in Chapter 5.

The plot of the phase angle against log |G*| (Black's representation of the complex plane) is presented in Figure 4.7. The benefit of such a plot is that it evaluates the performance of both models at the same time. As the viscoelastic behavior of asphalt binders can be predicted by these two functions, the results of the two proposed models

are presented against the experimental data for comparison. Figure 4.7 shows that predictions are reasonable.

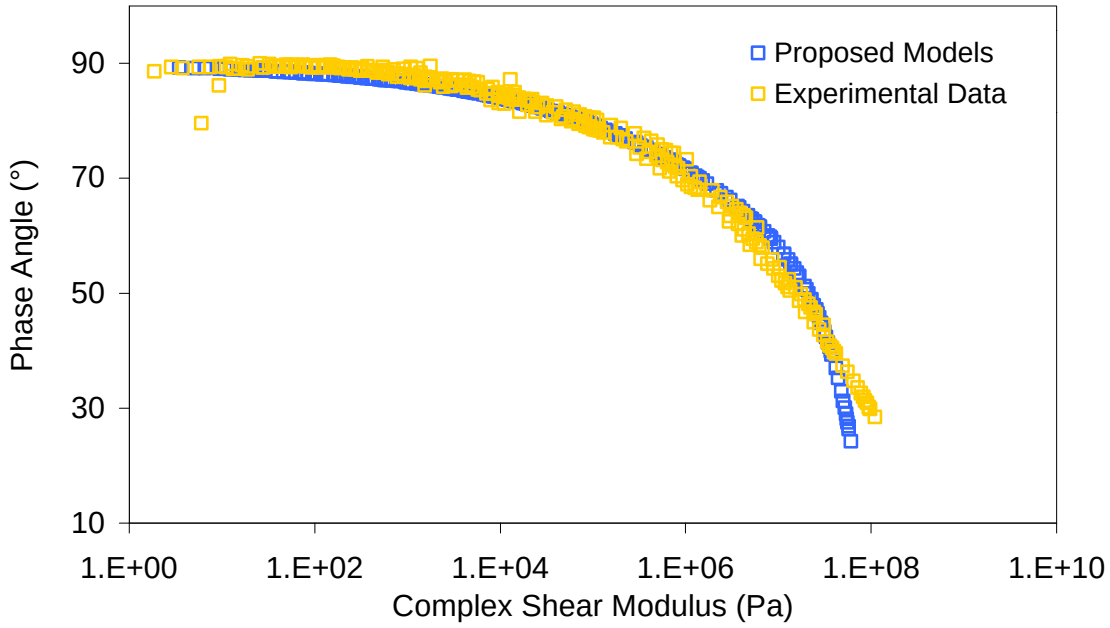

Figure 4.7. Black Diagram for PG 64-22U and Results of the Proposed Models

4.5. NON-LINEAR REGRESSION PROCEDURE

In order to obtain the model parameters, a non-linear regression method was needed. This was accomplished using the SAS (version 6.12) software package. The NLIN Procedure package offers different methods to perform a least-squares estimate of the parameters of a nonlinear model:

- Steepest-descent or gradient method
- Newton method
- Modified Gauss-Newton method
- Marquardt method
- Multivariate secant or false position (DUD) method

The Gauss-Newton and Marquardt iterative methods regress the residuals onto the partial derivatives of the model with respect to the parameters until the estimates

converge. The Newton iterative method regresses the residuals onto a function of the first and second derivatives of the model with respect to the parameters until the estimates converge (SAS, 1995). All these methods were tested in the beginning of this study, and the Marquardt method was selected for the following reasons:

1. The Marquardt method proved to be the most stable of the five methods: fast and good convergence resulted in most of the cases. Although this method requires the first derivative of the model with respect to the parameters, the adequacy of this method overcomes the cumbersome task of evaluating the derivatives.
2. The DUD method proved to be inadequate for the problem in hand, resulting in a poor convergence in most of the cases. This method might be useful for estimating quick starting values for the parameters.
3. The Newton and Gauss-Newton method take excessive time to converge. Also, the Newton method requires the specification of the second derivatives of the model with respect to the parameters.

The preliminary analysis of the data showed that the non-linear regression procedure is sensitive to the initial values of the parameters, and the software may fail to converge or converge to a local minimum if the initial parameters are wrongly selected. Also, the manipulation of the complex shear modulus (10 - 10^9 Pa) may result in an excessive accumulation of the error components resulting in overflows in computations. To address these possibilities, the model is presented in the logarithmic domain, resulting in the following model:

$$\log G^* = \log\left[G_g - \frac{G_g}{\left[1 + (w / w_0)^v\right]^w} \right] \tag{4.23}$$

which can be written as follows:

$$\log G^* = G_a + \log\left[1 - \frac{1}{\left[1 + (w / w_0)^v\right]^w} \right] \tag{4.24}$$

where,

G_a is equal to log G_g.

4.5.1. The Marquardt Method

For the system of Equations represented by the nonlinear model:

$$Y = F(\beta_0, \beta_1, \ldots\ldots, \beta_r, X_1, X_2, \ldots\ldots, X_n) + \varepsilon = F(\beta, X) + \varepsilon \qquad (4.25)$$

where X is a matrix of the independent variables, β is a vector of the parameters, ε is the error vector, and F is a function of the independent variables and the parameters. There are two approaches to solving for the minimum. The first method is to minimize

$$L(\beta) = 0.5\ (e'e) \qquad (4.26)$$

where, $e = Y - F(\beta)$.

The second method is to solve the nonlinear equations:

$$X'F(\beta) = X'e \qquad (4.27)$$

where,

$$X' = \partial F / \partial b \qquad (4.28)$$

In the nonlinear situation, both X' and $F(\beta)$ are functions of β and a closed-form solution generally does not exist. Thus NLIN uses an iterative process: a starting value for β is chosen and continually improved until the sum of squares error $\varepsilon'\varepsilon$ (SSE) is minimized. The iterative process begins at some point β_0 defined by the user. X and Y are used then to compute a Δ such that

$$SSE(\beta_0 + k\Delta) < SSE(\beta_0) \qquad (4.29)$$

The Marquardt method computes the Δ as follows:

$$\Delta = (X'X + \lambda \mathrm{diag}(X'X))^{-1} X'e \qquad (4.30)$$

The Marquardt method is considered to compromise between Gauss-Newton and steepest descent (Marquardt, 1963). As $\lambda \rightarrow 0$, the direction approaches Gauss-Newton. As $\lambda \rightarrow \infty$, the direction approaches steepest descent. An example of SAS input and output files is presented in Appendix A.