

THE UNIVERSITY OF CALGARY

Physical and Rheological Characterization of Selected Polymer Modified Asphalts

by

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Abstract

Asphalt is a multiphase colloidal system with asphaltene molecules dispersing in maltenes. In this work, physical and rheological methods have been used to assess the effect of polymers on the properties of asphalts mainly their high and low service temperature performance. SBS, SIS, and EVA polymers hot mixed with asphalt have shown a significant influence on the resistance of binders to permanent deformation at high pavement temperatures. Morphology/rheology of various binders modified with polymers was studied. Optical microscopy has yielded information on the microstructures. Time temperature superposition was found to be valid over large temperature/frequency ranges for these blends. Experiments using BBR indicated that no significant changes had taken place at the low pavement temperatures. The DMA has also been used to assess the glass transition temperatures of the PMA.

The binders modified with polymers can improve pavement performance. The level of improvement varies and depends on polymer type, polymer content, and processing conditions. Overall, the thesis revealed the importance of binders modified with polymer and some novel aspects in the glass transition temperatures. Large amount of studies still await researches to be conducted in order to fully understand this versatile asphalt binder.

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To the loving memory of my mother

Xuanjun Sun

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LIST OF SYMBOLS

a_T	Time-Temperature Shift Factor
C_1, C_2	WLF Equation Parameters
E_a	Activation Energy
G	Shear Relaxation Modulus
G'	Storage Modulus, Pa
G''	Loss Modulus, Pa
G^*	Complex Modulus (or Dynamic Modulus), magnitude in Pa
J^*	Complex Dynamic Compliance
m-value	Rate of Change of Creep Stiffness
$Pen_{25^\circ C}$	Penetration at 25°C, decimillimetre
R	Ideal Gas Constant
S	Stiffness Modulus, MPa
t	Time
T_g	Glass Transition Temperature
T_{high}	Highest Service Temperature, °C
T_{low}	Lowest Service Temperature, °C
T_{ref}	Reference Temperature in WLF Equation, K

Greek

δ	Phase Angle, rad
η	Steady Shear Viscosity, Pa.s or mPa.s
η'	Dynamic Viscosity
η''	Dynamic Storage Viscosity
η^*	Complex Viscosity
$\eta_{60^\circ C}$	Viscosity at 60°C, Pa.s
$\eta_{135^\circ C}$	Viscosity at 135°C, mPa.s
γ^*	Complex Shear Strain

γ	Strain
$\dot{\gamma}$	Shear Rate
σ	Stress
$\tau(t)$	Shear Stress at Time t
ν	Frequency, Hz
ω	Frequency, rad/s or Hz

Abbreviation

A0	Base Asphalt
B1	Binder Modified with 3% Radial SBS (Finaprene 411)
B2	Binder Modified with 5% Radial SBS (Finaprene 411)
B3	Binder Modified with 7% Radial SBS (Finaprene 411)
C1	Binder Modified with 3% Linear SBS (Kraton D1102)
C2	Binder Modified with 5% Linear SBS (Kraton D1102)
C3	Binder Modified with 7% Linear SBS (Kraton D1102)
D1	Binder Modified with 3% SIS (Kraton D1107)
D2	Binder Modified with 5% SIS (Kraton D1107)
D3	Binder Modified with 7% SIS (Kraton D1107)
E1	Binder Modified with 3% EVA (Elvax 150W)
E2	Binder Modified with 5% EVA (Elvax 150W)
E3	Binder Modified with 7% EVA (Elvax 150W)
F1	Binder Modified with 3% EVA (Elvax 350)
F2	Binder Modified with 5% EVA (Elvax 350)
F3	Binder Modified with 7% EVA (Elvax 350)

CHAPTER 1

Introduction

Asphalt was one of the first construction materials used by Man. Today, most asphalt used for road construction, asphalt-roofing felts, and for water and sound insulation applications, is produced by the petroleum industry.

The use of asphalt as a binder in the construction of pavements started at the beginning of the twentieth century. As a material for construction of pavement, asphalt plays a vital role in the development of modern society. The consumption of asphalts is now over 30 megatonnes every year in North America. In the United States, 85% of asphalt is used in road pavement (Asphalt Institute, 1989).

In the last decades, the high volume of road transportation combined with high stresses caused by heavy vehicles and an insufficient degree of maintenance started to lead to the rapid deterioration of pavements. To prevent this process, several types of measures may be effective, eg., improved pavement and mix design, better use of materials and more effective construction methods. Properties of materials in all layers of the road structure are of great importance for the life of the road. Several factors influence the performance of flexible courses, eg, the properties of the components (asphalt, aggregate and additive) and the proportion of these components in the mix. As a thermoplastic material, asphalt suffers from one important disadvantage: it is very sensitive to the temperature. Asphalt tends to become hard and brittle in cold weather, while in hot weather it softens and flows. The conventional materials used in the asphalt concrete mixture may perform satisfactory relative to one distress type but fail prematurely relative to the others. For example, pavements using hard binders will have low rutting potential, but they will have high fatigue and low-temperature cracking potentials. On the other hand, pavement with soft asphalt binders will have low fatigue susceptibility and low-temperature cracking resistance but high rutting behavior. In addition, the growing economic pressures lead to thinner pavement and deferred

maintenance. Therefore, the purpose of using special additives in an asphalt pavement is to achieve better road performance at extreme temperatures and heavy traffic loading.

The performance of the pavement is a function of pavement and mix design, quality of materials (asphalt and aggregates), subgrade conditions, traffic load, climate and maintenance. Any shortfall of one of these factors alone or in combination can cause distress or failure and result in shorter service life, poorer performance and/or increase in maintenance costs.

The main failure modes of pavements include plastic deformation, thermal cracking, fatigue cracking, ravelling and stripping. These failure modes are induced by the factors listed above, either alone or in combination.

Permanent deformation which includes rutting, shoving, and distortion occurs mainly at high pavement temperatures as well as at high axle loading and repeated loading. It is magnified by inadequate pavement design, poor workmanship, poor asphalt binders, mix design and water sensitivity. Using binders modified by polymers can make the binder stiffer and help to limit the plastic deformation (Lewandowski, 1994).

Thermal cracking occurs at low pavement temperatures. Thermal contraction induces tensile stress in the asphalt pavements. Hard and brittle binders with no capacity to deform, and low tensile strength are susceptible to thermal cracking.

Fatigue cracking mainly occurs at intermediate temperatures, higher than thermal cracking but lower than plastic deformation temperatures. It is the result of the accumulation of strains under repetitive loading over a long period of time. It also occurs as a result of low binder content, too hard a binder, water sensitivity and poor bearing capacity of the support layers.

There are several ways to minimize the pavement failures and to extend the service life:

- Developing new binder types with better engineering properties.
- Improving the pavement and mixture design.
- Mitigating deficiencies caused by aggregates.
- Improving the construction and maintenance techniques.

CHAPTER 2

Background

2.1 Composition and Structure of Asphalt

2.1.1 Composition of Asphalt

Petroleum asphalt is the heavy end product in the petroleum refinement. The yield can vary between 10 and 60 percent (Roberts, 1991) depending on the source of crude oil. The chemical composition of asphalt and its properties are largely dependent on the crude oil nature and its source. The 1991 survey showed that 120 different crude oils were used in United States to produce paving asphalt. According to Corbett (1984), several different crude sources are often mixed together to obtain asphalt binders for getting the required specifications.

Corbett (ASTM D4124) used selective adsorption-desorption chromatography to separate asphalts into asphaltenes (most polar), polar aromatics (strongly polar), naphthene aromatics (weakly polar), and saturates (non polar).

Asphalt is a mixture of multitude of compounds. However, even asphalts from different crude sources have similar elemental composition (Petersen, 1984). The major elements in asphalt are hydrogen and carbon, with oxygen, nitrogen and sulfur increasingly present at higher molecular weight fractions. Metal ions such as nickel, vanadium and iron are also present and they play an important role in the structure of asphalt (Corbett, 1969). Table 2.1 displays the elemental composition of asphalt binders.

Table 2.1 Elemental Composition of Asphalt Binders

Elemental	w (%)
Carbon (%)	82 – 87
Hydrogen (%)	9 - 11
Nitrogen (%)	0 -1.2
Sulfur (%)	0 - 6
Oxygen (%)	0 - 0.8
Vanadium (ppm)	0 - 1400
Nickel (ppm)	0 - 110

It is also known that asphalt is a complex disperse system in which asphaltenes are the dispersed phase and oils and resins are the dispersion medium (Yen, 1992; Boduszynski, 1979; Posadov and Rozental, 1985; Swanson, 1941).

In a common asphalt group analysis, asphaltenes are first precipitated by a minimum of 40 volumes of the liquid hydrocarbon, such as pentane or heptane. Insufficient volume of hydrocarbon may cause resins absorbing on asphaltenes (Speight, 1981). The soluble fraction, which is called maltene, can be further separated by solvent extraction or by chromatographic fractionation into saturates, naphthene aromatics and polar aromatics. Other separation method divides maltenes into oils and resins. The oils, resins and asphaltenes differ from each other in the solubility in liquid hydrocarbons and also in their molecular weight. The boundaries between the groups are undefined and the molecular weight and H/C ratio of these fractions overlap with each other (Speight, 1981, Selucky, 1981, Hall, 1981).

Oils contain the lowest molecular weight compounds of asphalt. The molecular weight ranges from 240 to 800, with most between 360 to 500. The C/H ratio is between 6.8 and slightly over 8.0 (atomic C/H of 0.55 to 0.68). Some heteroatoms such as O, N, and S might be present. The chemical structure of oils is mainly single or condensed

naphthene rings containing several side chains of varying length with alkyl side chains dominating. Alkylated aromatic hydrocarbons of very high boiling point may also be present. Oils usually contain much more side chains in the naphthenic-aromatic systems than resins. The hypothetical structure of oils is shown in Figure 2.1. Oils contain the most part of peptizing materials in asphalt; thus the content of oils mainly determines the hardness of asphalt.

Resins, besides oils, constitute the rest of maltenes. Propane and other lower boiling hydrocarbons can precipitate them. Resins are dark-coloured, heavy, semisolid or solid, very adhesive fractions of relatively high molecular weight. The molecular weight of resins obtained by chromatography ranges from 800 to 2000. The C/H ratio is between 8.3 and 9.6 (atomic C/H of 0.69 to 0.79). However, the ratio may vary significantly with the source of the crude oils. The O and S contents increase rapidly in the heavier resin fractions. Resins tend to contain longer alkyl side chains than asphaltenes. The hypothetical structures of heavier and lighter resin fractions are illustrated in Figure 2.2. Resins are also the dispersing medium for asphaltene colloidal system. Some researches believe that resins may form hydrogen bonding with asphaltenes and thus form the immediate film surrounding asphaltene in the whole multiphase colloidal system. Oils may further surround the resins to form the bulky peptizing medium.

Asphaltenes are usually precipitated by liquid hydrocarbons with a surface tension of 2.3 N/m^2 at 25°C or lower. The solvent used is either pentane or heptane. Asphaltene are dark brown to black friable solids without definite melting point (Speight, 1981). The C/H ratio of asphaltene varies from 8.4 to 10.4 (atomic C/H 0.7 to 0.85). Asphaltene also contain relatively large amounts of heteroatoms, such as O, N and S, as well as metal ions like nickel, vanadium and iron. The structure of asphaltene may contain an aromatic ring system with short side chains. Asphaltene are the highest molecular weight components of asphalt. The molecular weight of asphaltene varies significantly depending on methods of determination (Yen, 1992; Speight, 1985). The molecular weight of asphaltene may range from 2,000 (measured by vapour pressure

osmometry (VPO)) (Altgelt, 1968) to several tens of thousands or even hundreds of thousands (by ultracentrifugation method) (Winniford, 1963; Ray, 1957; Walas, 1964). These differences may be the result of the tendency of asphaltenes to form aggregates. When gel permeation chromatography (GPC) is used, the concentration of asphaltenes, temperature and the solvent used may influence the measured molecular weight of asphaltenes (Selucky, 1981). Boduszynski used field ionization mass spectrometry (FIMS) to determine the molecular weight of asphaltenes and to avoid the aggregation induced by electrostatic interaction between asphaltenes (Boduszynski, 1981).

2.1.2 Structure of Asphalt

It is generally agreed that asphalt is a multiphase colloidal system with asphaltene molecules dispersed in maltenes (oils and resins). Asphalt can be divided into three groups: sols, gels and sol-gels, according to its colloidal structure. The “gel” types are usually used as waterproofing materials, while “sol” and “sol-gel” types are suitable for the road construction (Zanzotto, 1987).

Because asphalt is considered to contain micelles, in which asphaltenes are surrounded by a protective layer of lower molecular weight hydrocarbons and are dispersed in oils, asphaltenes are the major components of asphalt. With regard to the structure of asphaltenes, there are two major hypotheses proposed by Speight and Yen (Speight, 1981; Yen, 1981), respectively. Speight and his coworkers proposed that asphaltenes are condensed, polynuclear aromatic ring systems with alkyl side chains. The number of aromatic rings may vary from 6 to 15-20. The hypothetical structure of an asphaltene molecule is shown in Figure 2.3. Speight suggested that asphaltenes may not aggregate, and that single asphaltene molecule is capable to form a micelle surrounded by a film of resins. Resins may interact with asphaltene molecules through electrostatic interactions as well as hydrogen bonding interactions. Such micelles can be further dispersed into oil medium to form the colloidal system.

Yen proposed a different model with regard to the asphaltene's structure. He suggested that asphaltenes have a skeleton of a peri-condensed system with aromatic rings (Figure 2.4). In contrast, the asphaltene structure he proposed is a little different from Speight and his colleagues. The major difference between his and Speight's model is that asphaltene molecule aggregate and the aggregates constitute the core of a micelle. He suggested that petroleum-derived asphaltene is not isotropic in structure. Many individually oriented clusters are suspended and randomly distributed with their lower molecular weight homologs. The individual clusters are ordered and consist of many planar aromatic molecules stacked in layers via the π - π association. X-ray diffraction data supported that the molecular weight for different units can vary substantially, with a unit sheet weight (1000-4000), a cluster or particle weight (4000-10,000) and a micelle weight (40,000-40,000,000). Furthermore, many of the aromatic parts of the sheet contain gaps or holes that can be used for the co-ordination of metal ions. As illustrated in Figure 2.5, many structural units can be formed in asphaltenes.

Although there is no agreement on the structure of asphaltenes, the above two hypotheses represent two main opinions. Yet, either of these two structures may not represent the real structure of asphaltenes. First, the asphaltenes studied may not be the original asphaltenes, because the extraction processes such as the distillation, solvent extraction and air blowing may alter the original structure of asphaltenes. Whether the structures derived from the experimental studies represent the authentic structures of asphaltenes is still not clear (Speight, 1981). Secondly, as mentioned above, the determination of the molecular weight of asphaltenes is problematic because of their tendency to aggregate. Although some researchers have adopted the diluted conditions, the conclusions obtained from these experiments may not reflect the real properties of asphaltenes. Thirdly, both of two structural models suggest two static structures of asphaltenes. In the multiphase colloidal system such as asphalt, structures may exist in a dynamic equilibrium (Selucky, 1981). For example, asphaltenes may disassociate and reassociate all the time in the colloidal solution. Thus Speight's model and Yen's model

may represent two extreme circumstances, a single asphaltene molecule and aggregates of asphaltenes, respectively.

As we have already mentioned, asphalt contains oils, resins and asphaltenes in a multiphase colloidal system. It is generally believed that asphaltenes are the core components in asphalt while oils and resins (maltenes) form the dispersing medium in the system. According to the intermolecular interactions between asphaltenes, asphalt can be divided into three classes. The first one is that single asphaltene molecules are dispersed in maltenes. Resins form a layer surrounding the asphaltene molecule through both electrostatic interaction and hydrogen bonding (Speight, 1981), and oils are the bulky medium that peptizes asphaltenes. In the second class of asphalt, two or three asphaltene molecules may connect with each other to form small aggregates that are then dispersed into maltenes. In this case, the concentration of asphaltenes is usually higher than that of the first class. The increase of the concentration of asphaltenes will favor the formation of asphaltene aggregates. The third class of asphalt will form in the presence of large amount of asphaltenes. Asphaltenes will connect with each other through intermolecular interactions to form an intricate network. Because of the relatively high concentration of asphaltenes and relatively low concentration of maltenes, this class of asphalt will be more brittle than the first two classes.

There are still a lot of debates on the exact structure of asphaltenes and asphalt. The best way to describe asphalt is as a substance composed of “complex hydrocarbons generally regarded as being colloidal in structure”. The difference in composition and molecular weight of asphalt is also related to the chemical nature of the original crude oil, the production technology. Although this thesis is focused on the physical and rheological properties of the polymer modified asphalt and conventional asphalt, it is necessary to have some knowledge of the chemical composition and structure of asphalt.

2.2 Performance of Asphalt in Service Temperature Range

Asphalt can be considered to be linear viscoelastic materials for engineering purposes (Monismith, et al., 1966). The stress vs. strain characteristics of asphalt is both time and temperature dependent. The balance between the viscous and the elastic nature of the asphalt effects the way particular asphalt behaves in pavement construction. According to the time-temperature superposition principle, in the linear viscoelastic region, which will be discussed later, asphalt behavior at higher temperatures and shorter loading time is equivalent to what occurs at longer loading time and lower temperatures. The behavior of asphalt at different service temperatures is discussed in the following sections.

2.2.1 High Temperature Behavior

At high temperatures (e.g., desert climate) or under sustained loads (e.g., slow moving trucks), asphalts act like viscous liquids and flow. Hot asphalt (at temperatures greater than 60 °C) is Newtonian fluid.

Hot asphalts are sometimes called plastic because once deformed, they do not return to their original position. This is why in hot weather, some less stable hot mix asphalt pavement flow under repeated wheel loads and rutting is formed in the pavement.

2.2.2 Low Temperature Behavior

At low temperatures (e.g., winter days) or very rapid loading times (e.g., fast moving trucks), asphalts behave like elastic solids. Elastic solids are like rubber bands. When loaded they deform, and when unloaded, they return to their original shape. Any elastic deformation is completely recovered. If too many loads are applied, elastic solids may break. Even though asphalt is elastic solid at low temperatures, it may become too

brittle and crack when excessively loaded. This is the reason “low temperature cracks” sometimes develop in asphalt pavements during the cold weather.

2.2.3 Intermediate Temperature Behavior

Most environmental condition lies between the extreme hot and cold situations. In these climates, asphalt binders exhibit the characteristics of both viscous liquids and elastic solids. This behavior of the asphalt is termed viscoelastic.

In order to understand the asphalt behavior in different service temperatures, the knowledge of rheological properties of asphalt is needed. Since asphalt can be treated as a mixture of low molecular weight polymers (Brodnyan, 1958; Lenz and Andrews, 1963), the methods of rheological study of polymers can be also applied to them.

2.3 Rheology of Asphalt

2.3.1 Linear Viscoelasticity

Rheology can be defined as a science dealing with the flow and deformation of various materials, where the flow is taken in a general sense. In this thesis, only small deformations are considered. According to (Kamran Majidzadeh and Herbert E. Schweyer, 1966), asphalts like many polymeric systems may be classified as linear viscoelastic materials when they are subjected to very low stress levels as compared to their ultimate strength. At the short time, their behavior is similar to that of an elastic solid (a glass), the long time behavior is similar to that of a viscous liquids, while at intermediate times their behavior contains elements of both extremes. At fixed time of loading, low temperatures lead to the short time behavior i.e. materials exhibit high stiffness and brittleness; whereas at higher temperatures the response shifts to the long time type behavior that is linked up with high ductility and exhibits low moduli (Jongepier and Kuilman, 1969).

Linear viscoelastic behavior depends on the temperature and time or the frequency of loading (Chartoff et.al., 1994). Although the non-linear properties are also related to the characterization of asphalts, a detailed discussion of that theory is beyond the scope of this thesis.

2.3.1.1 Stress and Strain

It is important to understand the stress-strain behavior in order to predict the engineering performance of any material. According to Van Der Poel (1965), for a given temperature and time of loading, the mechanical properties of bitumens can be expressed in terms of a stiffness modulus (S) defined as:

$$S = \frac{\text{Stress}}{\text{Strain}} \quad (2.1)$$

The stiffness modulus is analogous to Young's modulus for elastic solids, but it generally depends on the temperature and time of loading.

One of the most common tests for characterizing the stress-strain response of a material is the oscillatory test. The differences between elastic, viscous, and viscoelastic behavior are readily apparent in this test, as is shown in Figure 2.6 (Christensen, 1992). It follows from this figure, that an elastic material will exhibit stress in proportion to the strain, but not in proportion to the rate of strain. On the other hand, for viscous (Newtonian) fluids, when the load is applied, the material exhibits stress in proportion to the rate of strain but not to the amount of strain (Ferry, 1980; Bird et al., 1987). When a viscoelastic liquid such as asphalt, is forced to flow, it exhibits both elastic and viscous behavior and displays a time independent relation between an applied infinitesimal stress and the resultant strain.

One of the most important aspects of viscoelastic materials is that they exhibit memory in their response to stress or strain. For the linear materials, the relation between stress and arbitrary strain history, of the viscoelastic material, may be represented by mathematical models which are using hereditary integral representation (Ferry, 1980).

$$\tau(t) = \int_{-\infty}^t G(t-t') \frac{d\gamma}{dt'} dt' \quad (2.2)$$

Where $\tau(t)$ is shear stress at time t , $[\tau] = \text{Pa}$; $G(t-t')$ is the shear relaxation modulus at time $(t-t')$, $[G] = \text{Pa}$, and $\gamma(t')$ is the shear strain at time t' , $[\gamma] = \text{m/m}$.

2.3.1.2 Dynamic Mechanical Analysis

Although there are many methods of characterizing viscoelastic properties, dynamic (oscillatory) testing is one of the best techniques that can represent the behavior of the linear viscoelastic materials (Bahia, 1995). Normally, there are two different tests, which provide information regarding this class of materials. One is the strain controlled test performed on strain controlled rheometers, e.g. Bohlin (VOR) Rheometer. The sample is placed between two parallel plates in this test. The bottom plate oscillates to apply a sinusoidal strain to a specimen, and then the top plate transmits torque to a transducer that measures the stress as a function of frequency at a given temperature (Bird, 1987). When the temperature is low, the sample may behave almost as an ideal solid with phase angle being 0 degree. In contrast, at higher temperatures, when the sample is soft, most asphalts will behave as a Newtonian liquid (Verga et al., 1975). As a result, the phase lag between stress and strain is 90 degrees as for Newtonian liquids. A viscoelastic liquid will respond with a phase lag between 0 and 90 degree (Figure 2.7). The phase shift angle, also defined as the lag, is referred as δ (Goodrich 1987).

In the stress controlled dynamic mechanical analysis (e.g. Bohlin (CS) Rheometer), a sinusoidal stress is applied to the specimen, the top plate oscillates while the bottom plate is fixed, and the strain response is measured.

The phase shift angle is an important function for describing the viscoelastic properties of materials. In strain controlled dynamic testing, the phase angle $\delta(\omega)$ indicates the lag in the stress response compared to the applied strain. However, for the stress controlled testing, $\delta(\omega)$ represents the lag in the strain response compared to the applied stress.

Several material functions can be measured when dynamic testing is performed. The first one is the complex dynamic modulus, $G^*(\omega)$.

$$G^* = \frac{\tau(\omega)}{\gamma(\omega)} = \frac{\sigma_0}{\gamma_0} e^{i\delta} = \frac{\sigma_0}{\gamma_0} \cos \delta + i \left(\frac{\sigma_0}{\gamma_0} \sin \delta \right) = G' + iG'' \quad (2.3)$$

$$\text{i.e. } G' = \frac{\sigma_0}{\gamma_0} \cos \delta \text{ and } G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \quad (2.4)$$

Thus G^* is made up of two components, the storage modulus G' and the loss modulus G'' . In equation (2.3), $\sigma(t)$ is the stress, and $\gamma(t)$ is the strain, $\frac{\sigma_0}{\gamma_0}$ is the amplitude

$$\text{ratio, } \left(\frac{\sigma_0}{\gamma_0} = \sqrt{(G')^2 + (G'')^2} \right), \text{ and } \tan \delta = \frac{G''}{G'}.$$

A viscoelastic body is called linear if in harmonic oscillations the values of G' , G'' and δ are independent of the amplitudes of the stress and strain. They depend only on frequency ω .

In the shear load mode, the complex modulus ($|G^*|$) and the phase angle (δ) are measured. The $|G^*|$ represents the total resistance to deformation under load, while δ represents the relative distribution of that resistance between an elastic part and a viscous part (Bahia, 1995). Asphalt rheological properties are very sensitive to the temperature and the time of loading. At high temperatures or low frequencies, the δ value approach 90° , which reflects the approach to a viscous behaviour or complete dissipation of energy in viscous flow. On the other hand, the $|G^*|$ values decrease significantly, which reflects a decrease in resistance to deformation, asphalt becomes soft. As the temperature decreases or as the frequency increases, asphalts tend to approach a limiting value of δ zero degrees which reflects the completely elastic nature of the asphalts at these temperatures (Ferry, 1980) .

Another important material function is the complex dynamic compliance, $J^*(\omega)$, and it is used in the stress controlled dynamic testing.

$$J^*(\omega) = \frac{1}{G^*(\omega)} \quad (2.5)$$

where $[J^*] = \text{Pa}$.

According to the harmonic law (Vinogradov et al., 1980),

$$J' = \frac{\gamma_0}{\sigma_0} \cos \delta ; \quad (2.6)$$

and

$$J'' = \frac{\gamma_0}{\sigma_0} \sin \delta \quad (2.7)$$

Since $G^*J^*=1$, the relations between the components of the complex modulus and complex compliance are easily obtained.

$$G' = \frac{J'}{(J')^2 + (J'')^2} ; \quad (2.8)$$

$$G'' = \frac{J''}{(J')^2 + (J'')^2} ; \quad (2.9)$$

$$J' = \frac{G'}{(G')^2 + (G'')^2} ; \quad (2.10)$$

$$J'' = \frac{G''}{(G')^2 + (G'')^2} \quad (2.11)$$

A very important material function is the steady shear viscosity (η), which is defined as:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (2.12)$$

Where τ is the shear stress, and $\dot{\gamma}$ is the shear rate or the rate of deformation $[\dot{\gamma}] = \text{sec}^{-1}$.

It is possible to introduce the complex viscosity for harmonic oscillations as:

$$\eta^* = \frac{\sigma}{\dot{\gamma}} = \eta' - i\eta'' \quad (2.13)$$

where, $\eta' = \frac{\sigma_0}{\dot{\gamma}_0 \omega} \sin \delta$, and $\eta'' = \frac{\sigma_0}{\dot{\gamma}_0 \omega} \cos \delta$. The real part η' is called the dynamic

viscosity at frequency ω , and η'' is called the dynamic storage viscosity at frequency ω .

The relations between the components of the complex modulus and those of the complex viscosity are $\eta' = \frac{G'}{\omega}$; $\eta'' = \frac{G''}{\omega}$, and thus

$$|\eta^*(\omega)| = \frac{|G^*|}{\omega} = \frac{\sqrt{G'^2 + G''^2}}{\omega} \quad (2.14)$$

Where $\eta^*(\omega)$ is the complex viscosity, $[\eta] = \text{Pa.s}$. (Gownder, 1996).

According to the empirical Cox-Merz rule (Cox and Merz 1958),

$$\eta(\dot{\gamma}) = |\eta^*(\omega)| \text{ For } \dot{\gamma} = \omega \quad (2.15)$$

Where $\eta(\dot{\gamma})$ is the steady shear viscosity, and $\eta^*(\omega)$ is the complex viscosity.

For Newtonian liquids, the coefficient η depends also on the temperature and pressure. In non-Newtonian liquids, the viscosity depends also on the shear rate. The value of η at $\dot{\gamma}$ tending to zero can be called the zero shear rate viscosity or initial viscosity.

All complex characteristics, mentioned above, of a viscoelastic material depend on the frequency of harmonic oscillations.

Berker and Gilmore (1988) suggested that small amplitude oscillatory shear experiments are probably the most frequently used rheological methods to characterize the regular and polymer modified asphalts.

2.3.1.3 Time-Temperature Superposition

The time-temperature superposition principle was first advanced by Aleksandrov and Lazurkin in 1939. They found that the dynamic functions related to different temperatures are similar in their shape and can be superposed by shifting along the log-frequency axis. The amount of shift between different isothermal curves was named the shift factor, a_T . Using ωa_T as a variable, master curves can be constructed for the components of the complex shear modulus, $G'(\omega a_T)$ and $G''(\omega a_T)$ (Vinogradov, 1980).

Master curves based on the principle of time-temperature superposition are used as basic tools in analyzing dynamic mechanical data. Master curves rely on the principle of time-temperature superposition (Ferry, 1980). Master curves of G' , G'' , are generated from a wide range of temperatures and frequencies. One can first select the reference temperature, then shift all other temperature data horizontally until the curves overlap and

form a single, smooth master curve at the reference temperature. In practice, some minor vertical shifting may also be necessary. The shift factor depends only on the temperature, for a given system. There is a debate on choosing the right temperature dependence model for the shift factor. According to Bahia and Anderson (1993), the selection of the different temperature dependence models depends on the temperature and binder behavior. At high temperatures, typically 100 °C above the glass transition temperature, asphalt binders behave as Newtonian materials, and Arrhenius equation is selected. In the intermediate region, between the glass transition temperature and the Newtonian region (between T_g and $T_g+100^\circ\text{C}$), asphalt binders behave as simple linear viscoelastic materials, at small strains. In this case, the conventional Williams-Landel-Ferry (WLF) equation should be used. At low temperatures, below the glass transition temperature, asphalt binders behave as non-equilibrium systems, physical hardening predominates and affects the temperature dependency of asphalt binders, then the WLF equation is selected. However, Petersen et al., (1992) presented another opinion. They proposed that, in general, the WLF equations can be applied at temperatures above T_g and the Arrhenius function is suitable at temperatures below T_g . In principle, the shift factor should be the same for all viscoelastic functions (Ferry, 1980). The shift factors of asphalts studied in my thesis were found to satisfy both of these models. The Arrhenius relationship is given as follows:

$$\log a_T = \left\{ \frac{\Delta E_{ref}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right\} \quad (2.15)$$

where ΔE_{ref} is flow activation energy, kJ/mol, R is universal gas constant, and T_{ref} is reference temperature.

The Williams-Landel-Ferry equation (Williams et al., 1955) is given as:

$$\log a_T = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \quad (2.16)$$

where C_1, C_2 are the empirically determined coefficients, and T_{ref} is the reference temperature.

For comparatively small strains, asphalt modified binders can be considered to be linearly viscoelastic. For dynamic testing in the linear viscoelastic region, the time-temperature superposition principle is applicable. The results obtained at higher and lower temperatures can be equated graphically with lower and higher frequencies, respectively. Conversely, results obtained at higher and lower frequencies can be transposed into lower and higher temperatures, respectively.

2.3.1.4 Glass Transition Temperature

The glass transition temperature (T_g) is the temperature at which amorphous polymers change from a glassy state to fluid condition (Schmidt, 1966). Below T_g , material becomes brittle and glass-like without plastic flow (Schmidt et al. 1965). T_g is probably the most important parameter of an amorphous polymer (Tobolsky, 1960), and it has been considered as a reliable index for polymer characterization (Khong et al. 1978). Similarly important is T_g for the evaluation of the asphalt low temperature properties (Zanzotto et al., 1990).

As mentioned before, asphalts can be treated as viscoelastic, low molecular weight polymers. Thus T_g should be also an important parameter for regular and polymer modified asphalts.

There is no agreement on theoretical explanation of the glass transition temperature. The most common is the free volume theory, which defines the glass transition temperature as the temperature where the free volume of molecules decreases to such extent, that the molecules only vibrate, the rotational and translational movements

stop. At this state, the material has high elastic modulus and low viscous ability. The creep will occur once the temperature is raised (Ferry, 1980).

Other theories such as the thermodynamic theory and kinetic theory can also explain the glass transition temperature (Mark et al., 1984; Haward, 1973). T_g is usually considered predominantly as a rate and not equilibrium phenomenon (Wada et al., 1959). For example, Chartoff (1994) states that the transition region is rather narrow, covering about 15 °C for most linear amorphous polymers. It is also mentioned that the glass transition is considered as a kinetic transition or a relaxation transition because it is strongly influenced by the rate of cooling or the frequency of testing.

According to Chartoff et al. (1994), there are several factors affecting T_g in the dynamic mechanical analysis (DMA): instrumental factors, test frequency, material characteristics and the choice of T_g criterion. Instrumental factors are sample size, thermal gradients, temperature calibration and so on. Higher frequency will usually give higher T_g . The different specific thermal and mechanical history of the material belongs to material characteristics. T_g criterion is determined by the chosen viscoelastic functions, which is monitored during the experiment.

The dynamic mechanical measurements for viscoelastic characterization is very common since the data obtained from experiments are the two complementary functions showing both viscous and elastic material characteristics. The glass transition is generally identified from dynamic data, because the peak value of the loss modulus, G'' , is assumed to occur at T_g . The peak of $\tan \delta$ can also be chosen for the criterion of selection of T_g from DMA data. According to Chartoff et al. (1994), the peak loss modulus corresponds more closely to the “onset” of the glass transition shown in figure 2.8, while the peak of $\tan \delta$ value is more close to the transition midpoint. The “onset” temperature of T_g is determined by insertion of two targets to the storage modulus curve, one from the transition region and the other one from the glass region. As a result, the T_g from the peak of G'' is between the “onset” temperature and T_g from the peak of $\tan \delta$.

The temperature of the maximum loss modulus is the appropriate standard value (ASTM D 4065). According to ASTM D 4092, T_g is the appropriate midpoint of the temperature range over which the glass transition occurs.

It is assumed that change of the properties below the glass transition is one of the reasons which makes asphalts crack (Traxler et al., 1975), and T_g also appears to describe the cracking resistance at constant strain at low temperatures, (in fatigue,) better than the measured viscosities of asphalts (Schmidt, 1966). Note that some polymers show more than one T_g , depending on specific degrees of chain restriction (Schmidt, 1965). Chartoff, (1994) suggested that it depends on heating rates, if heating rates exceed 2 °C per min, double T_g artifact is observed. Such an effect was not observed in my investigations.

Various experimental techniques have been used to determine T_g . These are: differential thermal analysis (DTA), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and the dynamic mechanical analysis (DMA) — for studying the glass transition in polymers (Chartoff, 1994), asphalts (Khong et al., 1978; Schmidt et al., 1965), pitches (Rand et al., Barr et al., 1982), and bitumen-liquid rubber mixtures (Kortschot et al., 1984).

T_g has been widely used as the reference temperature in the Williams-Landel-Ferry equation (Williams et al., 1955) (3.17) which also gives the temperature dependence of the shear viscosity.

$$\log \frac{\eta(T)}{\eta(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (2.18)$$

where, T_g is the glass transition temperature; η is the steady shear viscosity and C_1 , C_2 are constants.

2.4 Polymer Modified Asphalt (PMA)

Polymers chosen as special additives in an asphalt pavement have a long history. As early as 1823, a patent for natural rubber added into tar was granted to English manufacturer Hancock (Zanzotto, 1987). In 1873, another patent for asphalt paving binder with one weight percent of latex (wt%) was granted to Samuel Whiting. In 1902, a French company first used the rubber modified asphalts on the pavement roads (Thompson, 1979). Since the World War II, more and more polymers have been used in asphalt pavement to improve the road performance, increase the service life of the pavement, meet the heavy traffic demands, and save costs of maintenance. According to a survey conducted in 1994, over 40 million pounds (18 million kilograms) of styrene/butadiene type polymers were used for paving asphalt modification (Lewandowski, 1996). Ponniah and Kennepohl (1996) reported that, the incremental life-cycle cost analysis showed that the PMA is cost-effective, providing that the cost of PMA does not exceed the cost of conventional asphalt by more than 100%. PMA are therefore chosen to reduce life cycle costs in many cases. In the present, some new techniques, including microsurfacing or using emulsion chip seals on heavy traffic roads have been applied to modified binders. It is realized that binders often require modification to meet the needs for low temperature resistance to thermal cracking, and high temperature resistance to rutting. It is predicted that more and more polymer modified bitumens will be used for specific applications in the near future because of their outstanding performance.

Several reasons lead to the recent growth in polymer modification (Anderson, 1990).

1. The increasing traffic-related problems demand improvement.
2. Some waste materials and excess supplies of industrial byproducts are converted to asphalt additives. e.g., use of asphalts from crude oils with the yield of asphalt of poorer quality.
3. The growing economic pressures lead to thinner pavement and deferred maintenance.

2.4.1 Types and classification of polymers

Unlike asphalt binders, a polymer contains a large amount of atoms, and is formed by the successive linking of one or more types of small molecules (monomers) into long chains, clusters or network structure (Hall, 1985). King, Muncy, and Prudhomme (1986) defined polymers as large molecules composed of a repetition of smaller, normally organic, structural units called monomers. There are three proposed mechanisms in the production of polymers. One is the polymerization in which the main molecular chain contains only carbon atoms. The second is polycondensation in which the main molecular chain also contains atoms other than carbon, for example, oxygen, nitrogen, sulfur. The third is polyaddition. Sometimes all three are called polymerization (Zanzotto, 1987).

From the point of view of asphalt modification, modifiers can be divided into two groups: elastomer and plastomer. An “elastomer” is a polymer, such as styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS), which exhibits elastic or rubbery characteristics. When stretched and released they will tend to recover their original shape and size and make the binders more flexible and resilient. A “plastomer” is a polymer, such as low-density polyethylene (LDPE), which can form a tough, rigid network. These polymers display high strength to resist heavy loads, but may crack when strained because they demonstrate plastic-like properties. When stretched and released they are marked by irreversible deformation. Both groups are thermoplastic, i.e., they flow like viscous liquids at elevated temperatures.

According to Zanzotto (1987), some thermoplastic rubbers, e.g. SBS (or SIS) block copolymer, due to their unique molecular structure, behave like cross-linked elastomer at low temperatures (below approximately 100 °C). “Because their cross-linking is due only to physical forces and is reversible with an increase in temperature, their contribution to asphalt viscosity at technological temperatures is acceptable.”

Elastomeric polymers usually have a better impact on asphalt properties and are more compatible with asphalts when compared with plastomers. The cost of elastomers is higher than that of plastomers.

2.4.2 Selection of Polymers

Recent studies demonstrated that the properties of binders could be improved significantly and economically by using 3% to 6% polymer modifiers (Zanzotto et al., 1987). The most important goal in selecting a modifier is to make the asphalts less stiff in cold weather, and stiffer or more viscous in hot weather. Well performing modified asphalt should have also improved fatigue resistance and water sensitivity.

According to Zanzotto et al., (1987) the selection of the correct modifier can:

1. Lower the temperature susceptibility of asphalt in the range of -40°C to $+60^{\circ}\text{C}$.
2. Lower the loading time susceptibility of asphalts.
3. Increase the resilience of asphalts.
4. Improve cohesion and adhesion of asphalts.

Polymers are selected as bitumen modifiers in order to achieve improvement of the asphalt concrete pavement. Ideal modifiers should have the following properties: firstly, these polymers have to be compatible with asphalts, secondly, they have to keep its properties in storage and service life after mixed with asphalts, thirdly, they must not degrade during mixing, fourthly, they have to reduce the temperature susceptibility (Zanzotto et al., 1989).

Selecting the base asphalt is as important as the polymer selection. According to (Ponniah and Kennepohl, 1996), the soft grade base asphalt used for blending polymers can have its resistance to plastic deformation increased without affecting the low temperature performance of asphalt pavements. The final performance of polymer/asphalt blend is determined by the chemical nature, the concentration, the

molecular weight of polymers as well as the refining process, the crude source and the grade of the base asphalt employed.

Above all, the modifiers available on the current market are new to the industry and therefore do not have a substantial performance history. There is no clear guidance available on selecting modifiers for a given set of conditions and performance requirements.

2.4.3 Hot Mix of Polymer/Asphalt Blends

There are several ways for polymers to be added into to asphalts. In the field, one of the very useful techniques is in-line blending of polymer into the asphalt feed line. Another technique is pre-blending polymer at the asphalt terminal, refinery, batch plant and drum plant operations (The Asphalt Institute, 1989).

In the laboratory, high shear mixer is usually used for blending polymers and asphalt at temperatures between 160 °C and 180 °C for about one and half hours. If low shear mixer is used, the longer mixing time is needed. There are three crucial aspects to be met in hot mix technologies: compatibility (stable dispersion); thermal stability; and workability of polymer and asphalt mixtures (Zanzotto et al., 1989).

2.4.3.1 Compatibility

Compatibility can be defined as the state of dispersion between two dissimilar components (Lu and Isacson, 1997). The compatibility of PMA is the result of the mutual effects between polymer and asphalt (Zanzotto, 1987). A polymer/asphalt network is generally a function of many variables including : asphalt composition; chemical structure of polymer (e.g. block copolymer, SBR latex, and etc.); polymer concentration; polymer molecular weight; the physical properties of the polymer; the nature of the interactions between polymer and asphalt; asphaltene content in asphalt and

the thermal mechanical history of the blend such as the mixing time, shear rate, and the temperature (Kortschot and Woodhams, 1984; Lewandowski, 1994).

Microscopy is often used to determine the compatibility of polymer modified asphalt blends. The most common analytical technique is the fluorescence optical microscopy (FOM) (Bouldin et al., 1990; Lu et al., 1997). Frequently used are also the scanning electron microscopy (SEM) (Bhurke et al., 1997) and the scanning transmission electron microscopy (STEM) (Bouldin et al., 1990).

The blending can yield the three different types of morphology in polymer/asphalt after the hot mixing.

The first type: the mix is completely homogenous, this case rarely occurs. In this case, the oils in the bitumen completely solvate the polymer. Although the modified binder is absolutely stable, the binder mechanical properties including elasticity and tensile strength change little only viscosity increases (Lu et al., 1997).

The second type: the mix is heterogeneous, this is the case of the so called incompatibility since the bitumen and the polymer are separated.

The third type: the mix is micro-heterogeneous (Brule, 1996), and is made up of two distinct finely interlocked phases. This case is most important, it represents the so called compatibility. Compatible polymer “swells” by absorbing some of the oily fractions of the bitumen to form a polymer phase distinct from the bitumen phase including the rest of the oils, plus the resins and asphaltenes.

The morphology of polymer modified asphalt binders can also be divided into three critical groups depending on the concentration. First group is asphalt mixed with up to three weight percent polymer (wt%). In this group, the polymer phase is dispersed in the bitumen continuous phase. The second group, the concentration of polymer is up

to 5%, the two phases are continuous and interlocked. This kind of system normally has stability problem. The last one, the polymer content is 7% or more, i.e., the polymer content is relatively high. The polymer plastified by the oils of bitumen becomes continuous phase, while bitumen that includes heavier fractions (resins, asphaltenes and the rest of the oils) becomes dispersed phase. This system should be termed as an adhesive instead of a polymer modified bitumen (Brule, 1996). Those three groups also depend on the molecular weight of the polymer.

Considerable amount of research was performed on polymer/asphalt morphology and its related properties to modified binders. Lu and Isacsson, (1997); Stroup-Gardiner, (1998) and Rogge et al., (1989) stated that the viscoelastic properties of a polymer modified binder are influenced by the morphology of the system. A binder with quasi homogeneous morphology, which can be obtained with a short blending time or using a low-shear mixer (Van Gooswilligen and Vonk, 1986), generally will give good viscoelastic properties.

By using fluorescence optical microscopy (FOM) and gel permeation chromatography (GPC) techniques, Lu et al. (1996) found that the degree of SBS dispersion in bitumen affects the storage stability and the viscoelastic properties of PMA binders. According to his research the low compatibility may result in poor storage stability, which leads to separation of polymeric and bitumenous phases and inconsistent binder quality.

Stroup-Gardiner (1996) observed that when the polymer is discretely distributed within the asphalt, the loss factor ($\sin \delta$) will reflect the properties of the unmodified asphalt.

2.4.4 Influence of Morphology on Rheological Properties

When the linear viscoelastic functions are plotted against time (or the dynamic functions are plotted against frequency), the logarithmic scales have to be used because

of the large range and the domain of these functions. Inspection of these log-log plots reveals a pattern of certain zones on the time (or frequency) scale, where the viscoelastic functions have characteristic shapes. Those are: the transition zone from glass-like to rubber-like consistency, the plateau zone, the pseudo-equilibrium zone (some cross-linked polymers), the terminal zone, etc. These regions can be associated with different types of molecular response, and they appear with different degrees of prominence. For example, Tuminello (1986) gives the following example of the master curve of the storage modulus ($G'(\omega)$) for a typical linear amorphous polymer (shown in Figure 2.9).

2.4.5 Advantages of PMA

The ideal asphalts modifier would contribute to following:

- Lower stiffness at cold ambient temperatures, to reduce cracking.
- Higher stiffness at high temperatures, to reduce rutting and shoving.
- Improve adhesion of asphalts to aggregates in the presence of moisture to reduce the stripping.

The ideal behavior of binder is only theoretical and it can not be reached in practice (Zanzotto et al., 1990). The biggest real advantage in using polymer modified asphalt is changing the rheology of asphalts. Polymer modification leads to significant changes in the stress-strain behavior as well as the creep responses. The ability of some polymers to elastically recover gives added durability to asphalts, and it also expands the range of service temperatures.

When an asphalt is modified, the viscosity at 60 °C changes dramatically. The increase of viscosity will improve the binder-aggregate adhesion (Choquet and Ista, 1992). It will also improve the resistance to plastic deformations.

PMA can be applied wherever extra durability and performance are required. This is due to their improvement in resistance to thermal cracking, fatigue damage, rutting,

stripping and temperature susceptibility.

PMA is used in all paving and maintenance applications, i.e. hot mix, cold mix, recycling, hot and cold crackfilling, patching, chip seals and slurry seal (The Asphalt Handbook, 1989).

2.5 SUPERPAVE™ Specification

Owing to the complexity of both phases (polymer and asphalt), the characterization and study of PMA is quite complex. An agreement has not been reached on the type of tests and specifications to be used for PMA. The empirical tests are not accurate enough for the studying the PMA, particularly at high and low temperatures. The performance-based Strategic Highway Research Program (SHRP) specification tests and rheological tests are used to foresee PMA performances.

The Strategic Highway Research Program (SHRP) was funded by an allocation of one-fourth of one percent of federal funds allocated for highway construction in 1987, or approximately \$150,000,000, and was divided into four sections as follows:

- | | |
|---------|---------------------------|
| A – 001 | Project Co-ordination |
| A – 002 | Chemistry of Asphalt |
| A – 003 | Asphalt Aggregate Mixture |
| A – 004 | Asphalt Modifiers |

In 1991, SUPERPAVE™ was termed to signify the integration of performance-based specifications, and it became the final product of SHRP asphalt research program.

The Superpave binder specification and the test methods used to characterise asphalt in it are evaluated in both AASHTO (American Association of State Highway Transportation Officials) and ASTM. The Superpave tests measure physical properties that can be related directly to field performance by engineering principles. The Superpave binder tests are also conducted at temperatures that occur in pavements during service.

Table 2.2 lists the test equipment and a brief description of each test in SUPERPAVE™ specification.

Table 2.2 Superpave Binder Test

Equipment	Purpose
Rotational Viscometer (RV)	Measure binder flow properties at high temperatures
Rolling Thin Film Oven (RTFO)	Simulate binder aging (hardening) characteristics
Pressure Aging Vessel (PAV)	Simulate binder aging (hardening) characteristics
Dynamic Shear Rheometer (DSR)	Measure binder permanent deformation (rutting) and fatigue cracking at high and intermediate temperatures
Bending Beam Rheometer (BBR)	Measure binder thermal cracking at low temperatures
Direct Tension Tester (DTT)	Measure binder thermal cracking at low temperatures
Flash Point	For the safety purpose

The central theme of the Superpave binder specification is its reliance on testing asphalt binders in conditions that simulate the three critical stages during the binder's life. Tests performed on the original asphalt represent the first stage of transport, storage, and handling. The second stage represents the asphalt during mix production and construction and is simulated for the specification by aging the binder in a Rolling Thin Film Oven. This procedure exposes thin binder films to heat and air and approximates the aging of the asphalt during mixing and construction. The third stage occurs as the binder ages over a long time period as part of the hot mix asphalt pavement layer. This stage is simulated for the specification by the pressure aging vessel. This procedure exposes binder samples to heat and pressure in order to simulate years of in-service aging in a pavement.

In SUPERPAVE™ specification, performance graded (PG) binders are selected based on the climate in which the pavement will serve. The distinction among the various binder grades are the specified highest and lowest temperatures at which the

requirements must be met. The highest temperatures are obtained from the laboratory testing on the dynamic shear rheometer (DSR), and the lowest temperatures are obtained from the bending beam rheometer (BBR). The current binder grades in AASHTO MP1 are listed in Table 2.3.

Table 2.3 Superpave Binder Grades

High Temperature Grades (°C)	Low Temperature Grades (°C)
PG 46	-34, -40, -46
PG 52	-10, -16, -22, -28, -34, -40, -46
PG 58	-16, -22, -28, -34, -40
PG 64	-10, -16, -22, -28, -34, -40
PG 70	-10, -16, -22, -28, -34, -40
PG 76	-10, -16, -22, -28, -34
PG 82	-10, -16, -22, -28, -34

If a binder is classified as a PG 58-28, it means that the binder will meet the high temperature physical property requirements up to a temperature of 58 °C and low temperature physical property requirements down to -28 °C. The performance graded asphalt binder specification is in APPENDIX 1.

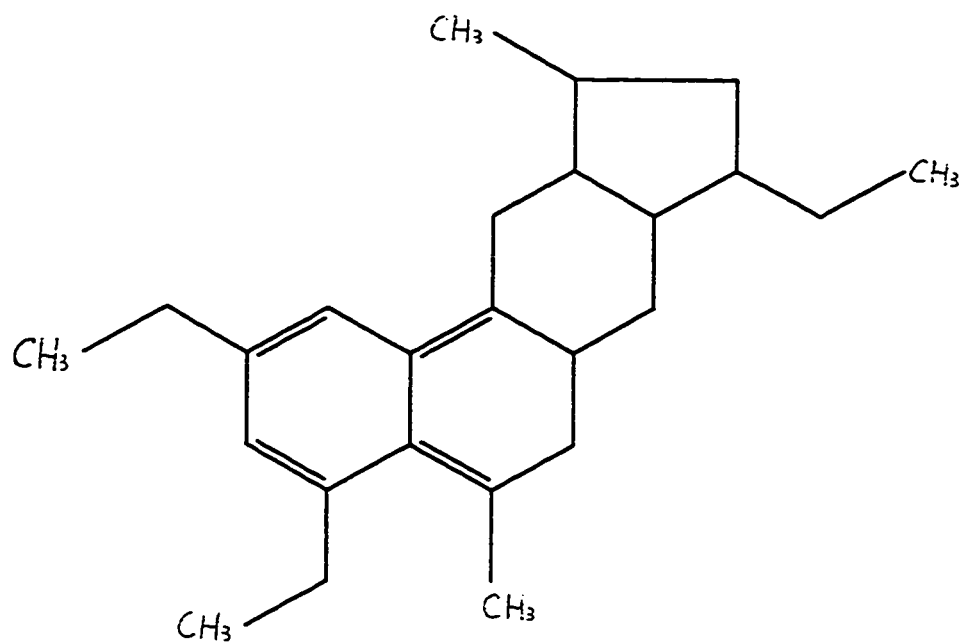


Figure 2.1 Hypothetical Structure of a Closely Separated Lubricant from Ponca City Petroleum

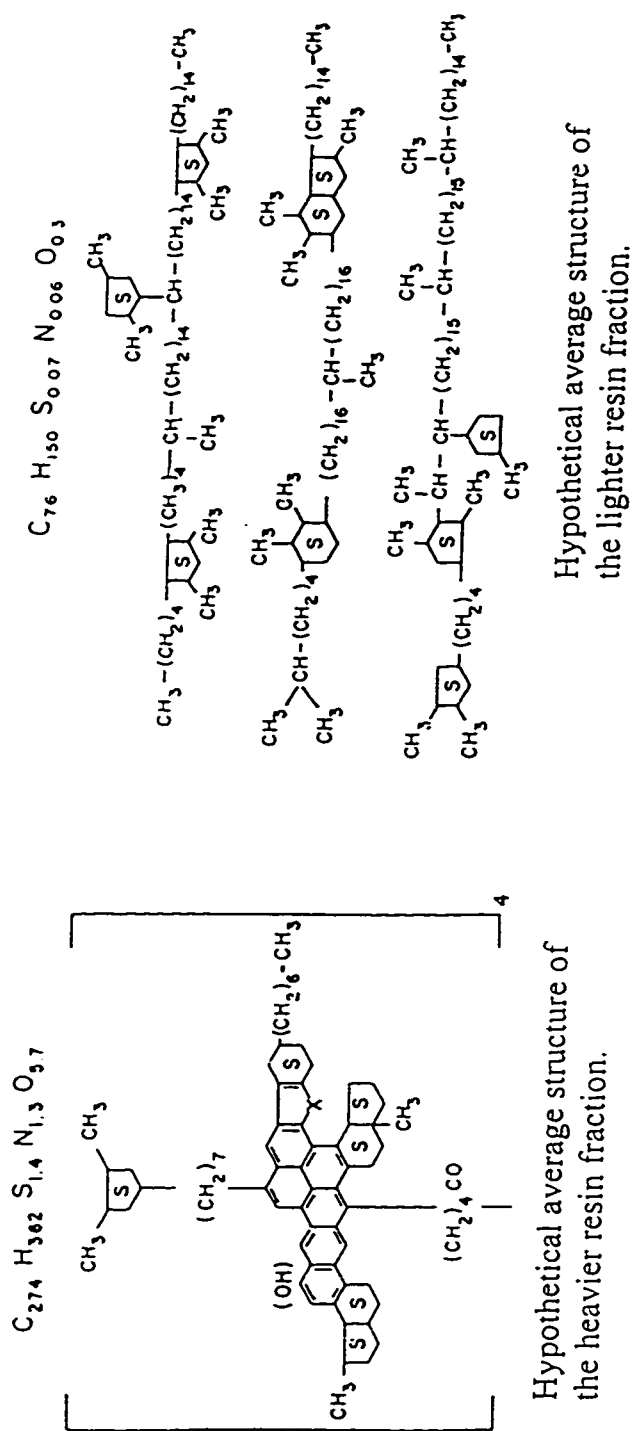


Figure 2.2 The Hypothetical Structures of Heavier and Lighter Resin Fractions

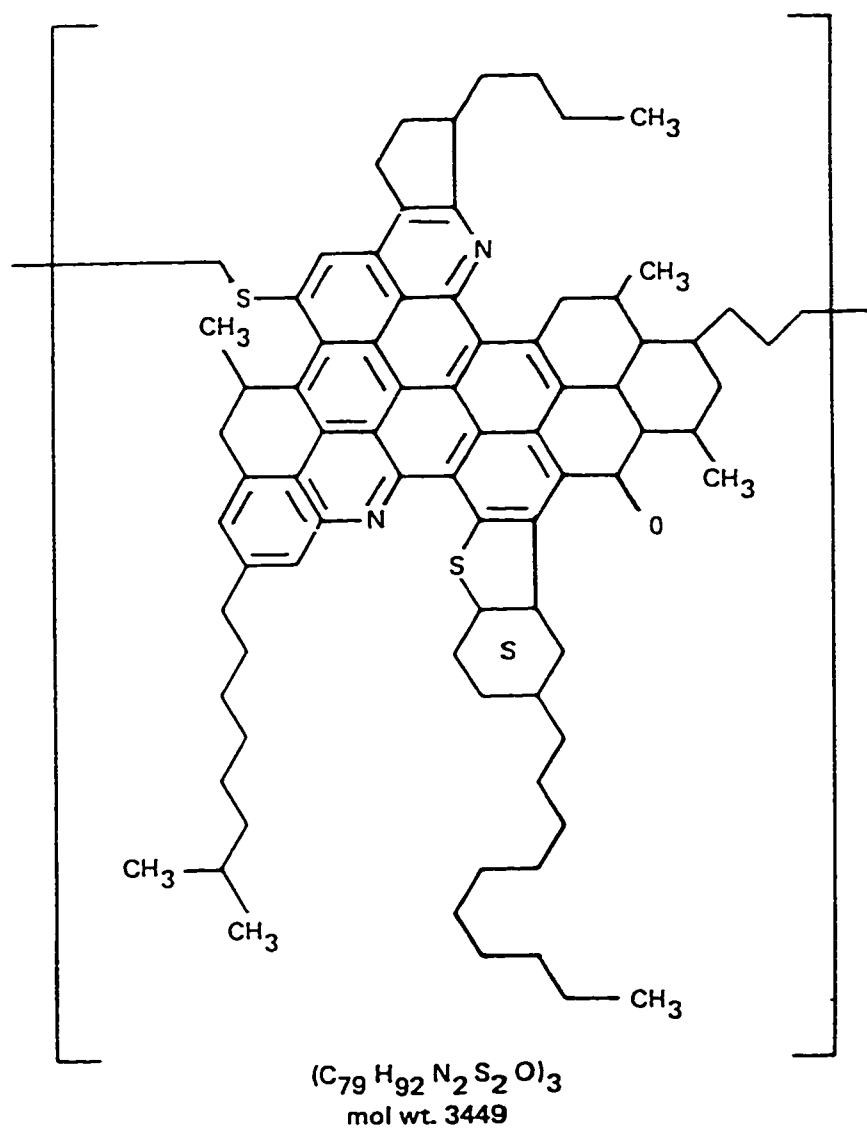


Figure 2.3 The Hypothetical Structure of A Petroleum Asphaltene

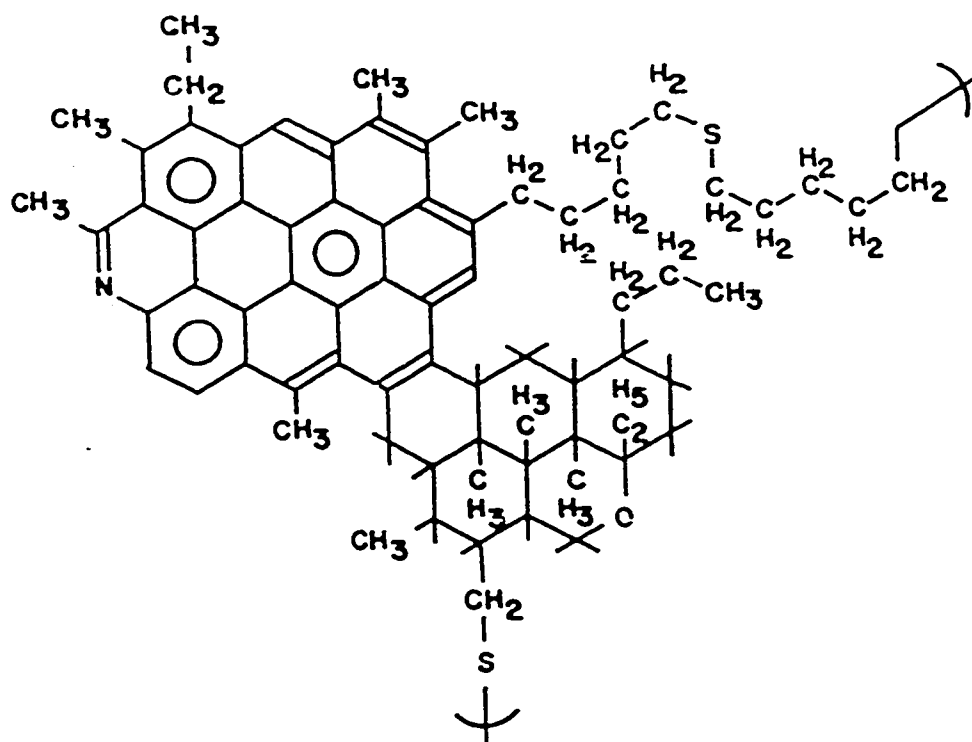
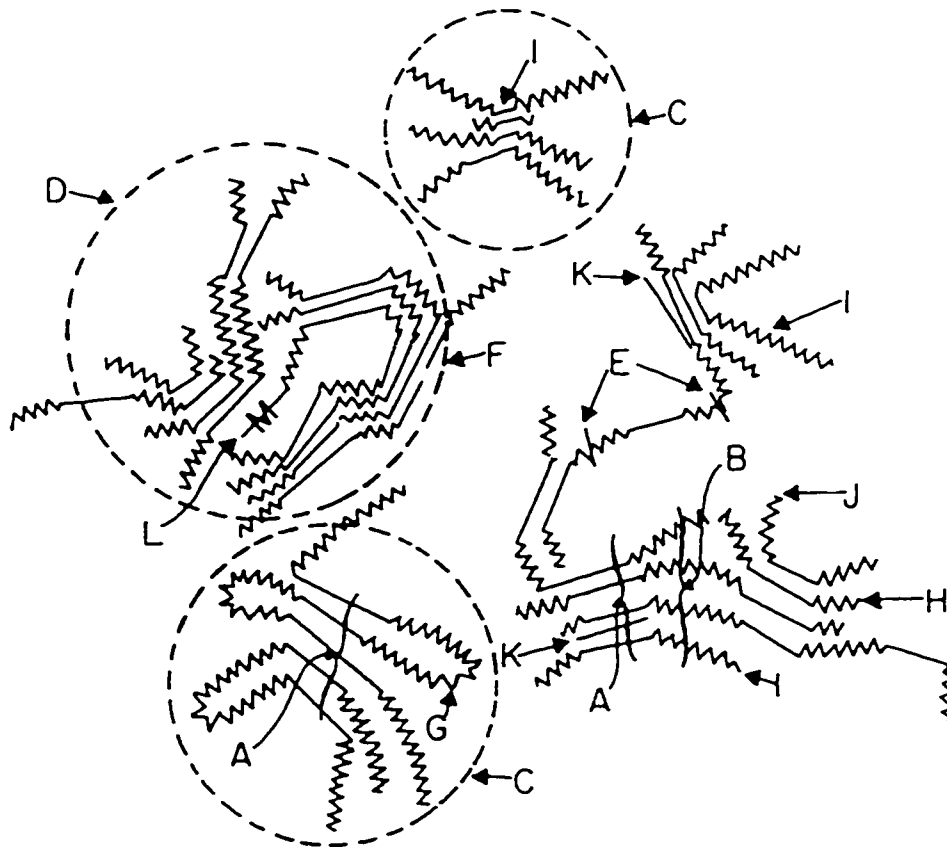


Figure 2.4 The Hypothetical Structure for A Laquinillas Asphaltene



Macrostructure of Asphaltics

- | | |
|-------------------|-----------------|
| A. Crystallite | B. Chain Bundle |
| C. Particle | D. Micelle |
| E. Weak Link | F. Gap and Hole |
| G. Intracluster | H. Intercluster |
| I. Resin | J. Single Layer |
| K. Petroporphyrin | L. Metal (M) |

Figure 2.5 The General Features of the Macrostructure of Petroleum-Derived Asphaltenes and Related Substances

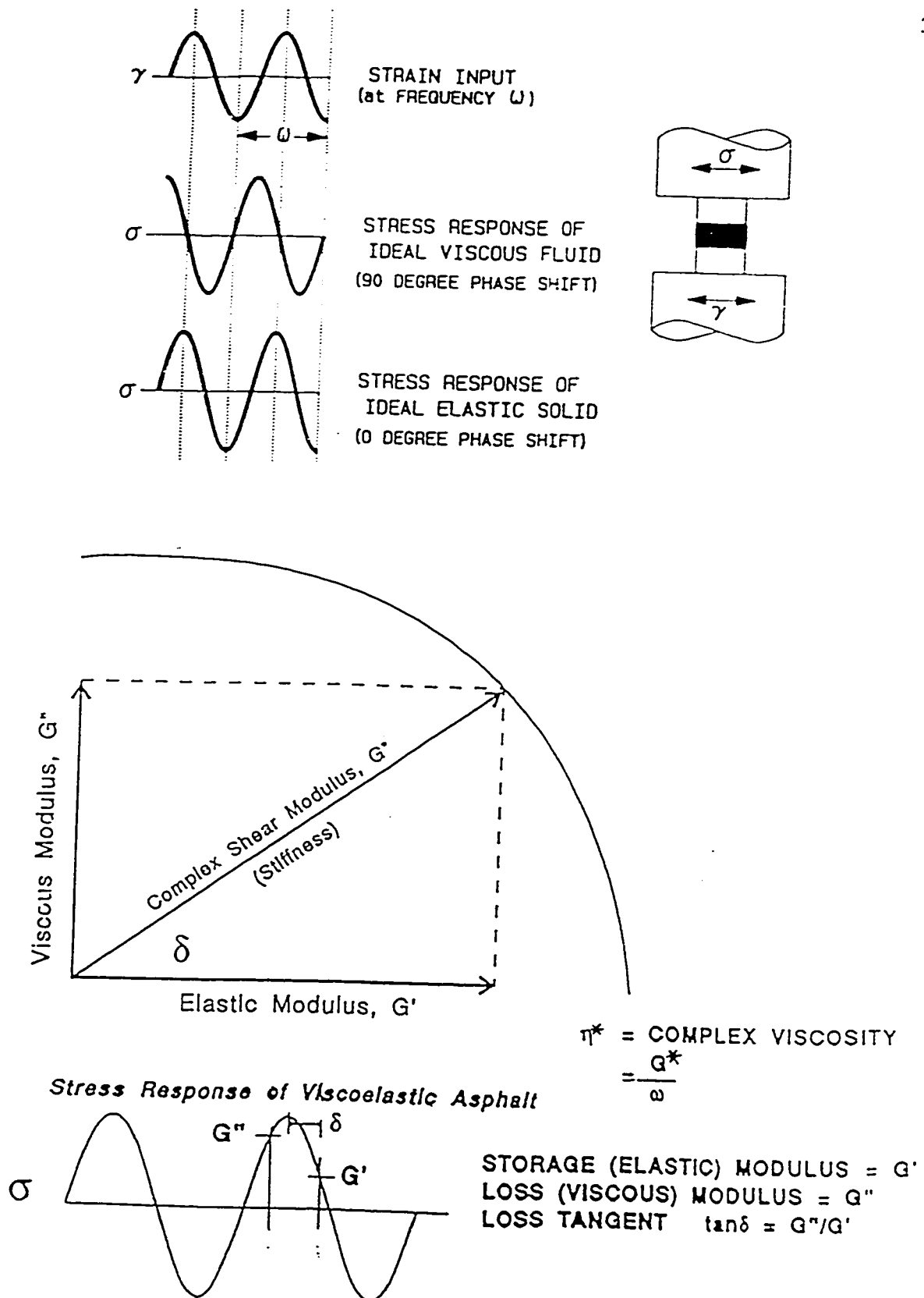


Figure 2.6 Dynamic Mechanical Analysis

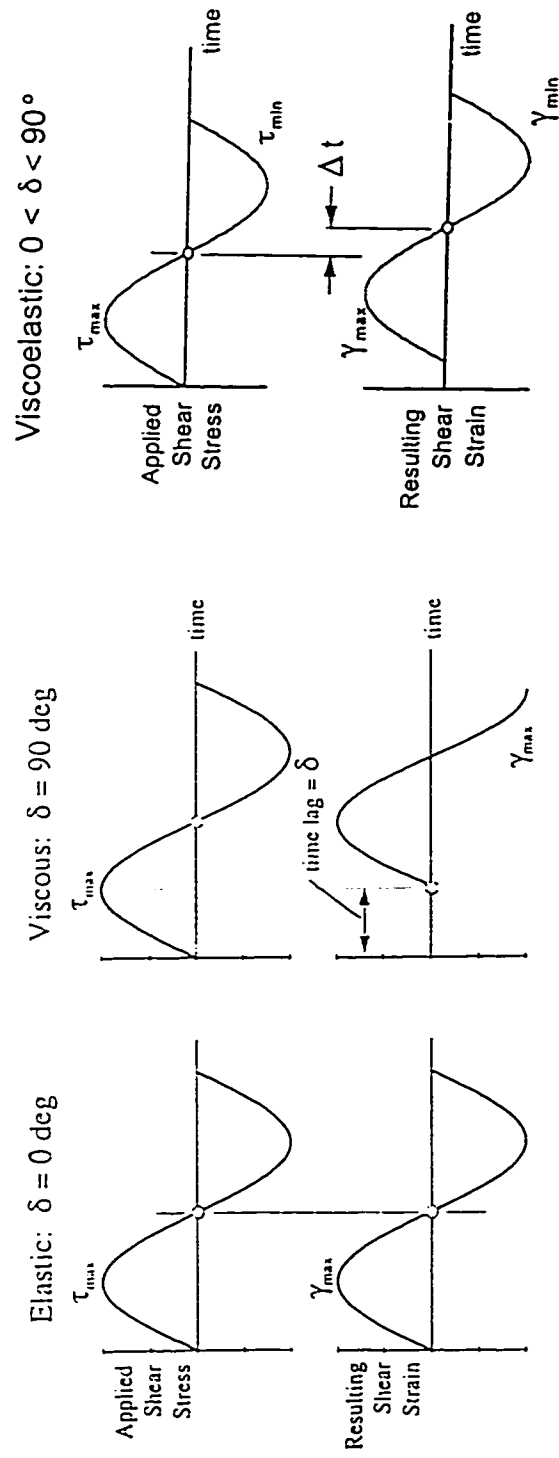


Figure 2.7 The Phase Lag of Elastic, Viscous, and Viscoelastic Material's

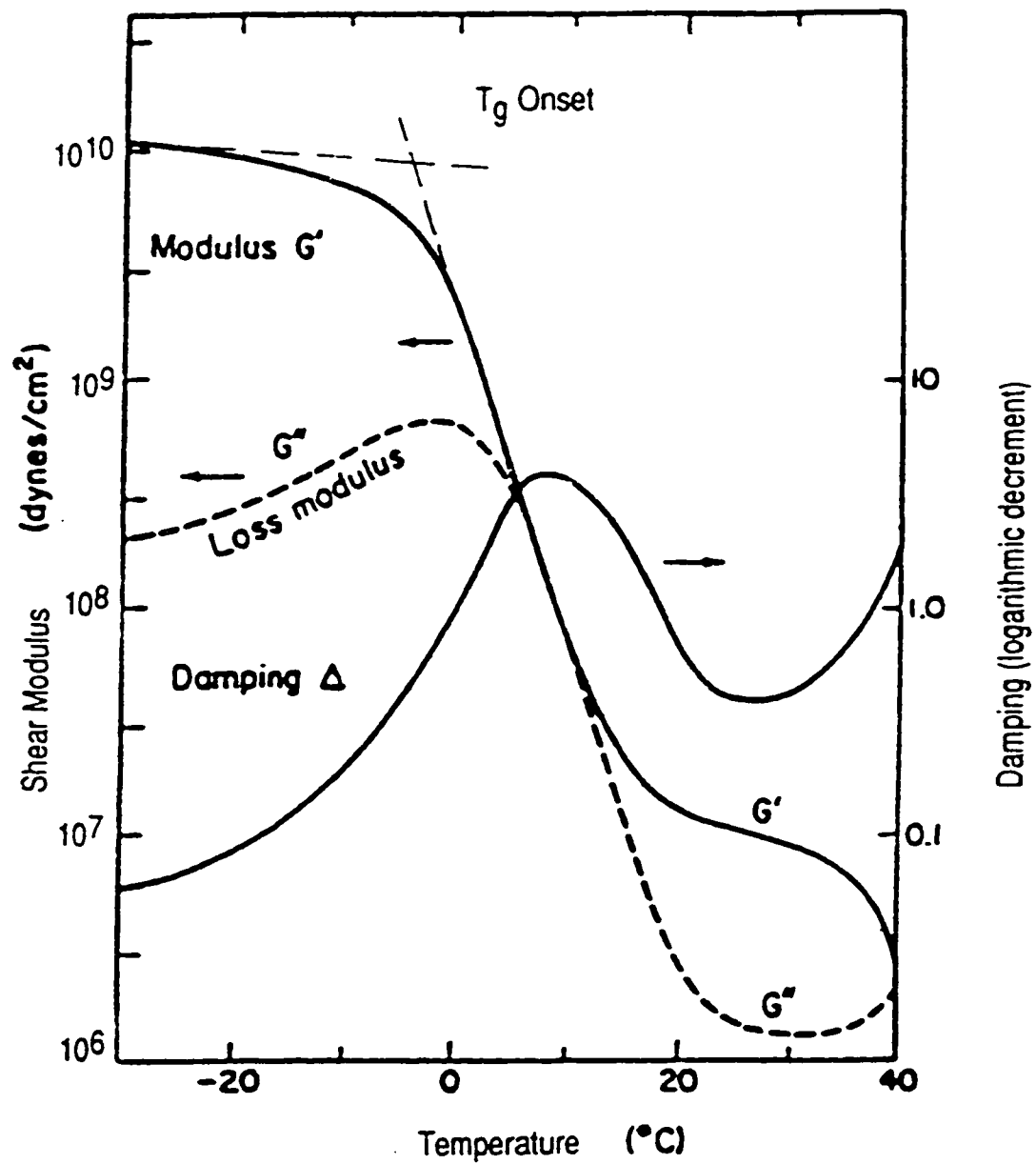


Figure 2.8 Typical Dynamic Mechanical Behavior for Viscoelastic Functions, G' , G'' , and $\tan \delta$, Data Taken at Frequency 1 Hz

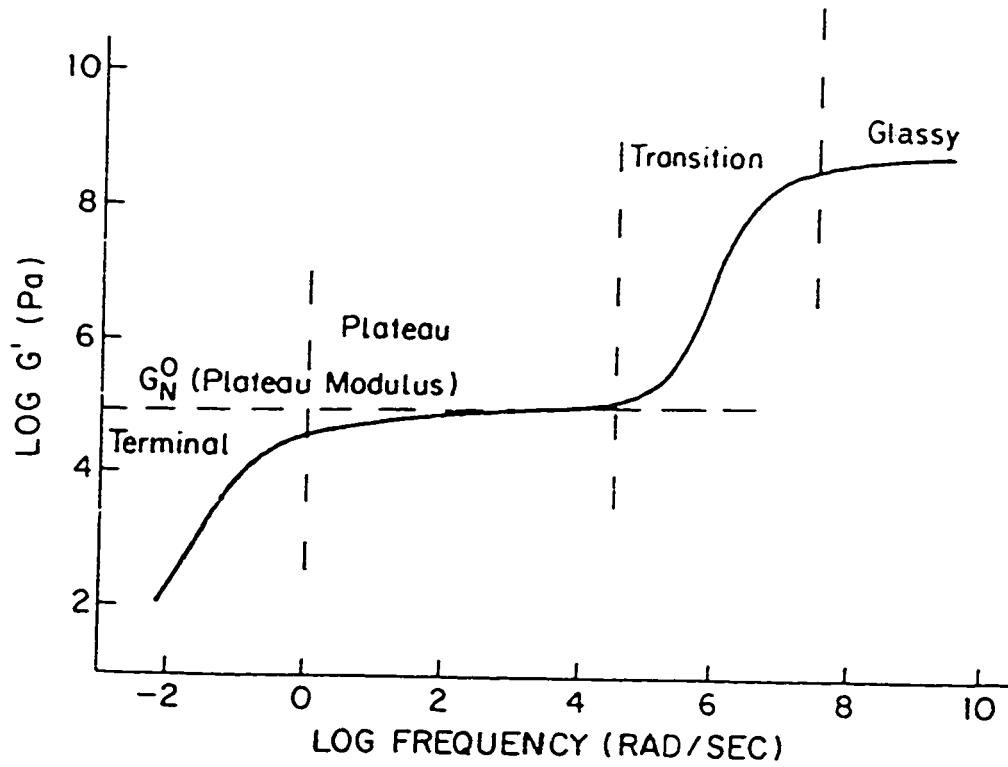


Figure 2.9 G' Mastercurve for A Typical Linear Amorphous Polymer

CHAPTER 3

Objectives of the Research

This thesis deals with binder performance and improvement of the binders through the addition of modifiers. Asphalt modifiers have been used to improve the properties of asphalts over the last 50 years (Wardlaw and Shuler, 1992). The most important goal in selecting a modifier is to make the asphalts less stiff in cold weather, and stiffer or more viscous in hot weather. In Canada, a large percentage of asphalt pavement failures occur because of extremes in ambient temperatures, which forces asphalt to perform in extremely large range of service temperatures.

3.1 Scope of Research

Recent studies demonstrated that the properties of binders could be improved significantly and economically by using 3% – 6% polymer modifiers (Zanzotto et al. 1987). Thus this research project concentrates on polymer modification of asphalt binders. The objectives of the research project were:

1. Review the literature on chemical composition, structure, and rheology of asphalts, as well as polymer modified asphalt (PMA).
2. Select the asphalts and the polymers for testing.
3. Define the physical, and rheological properties desired in different polymer modified binders.
4. Use SHRP PG specification to test properties of modified binders for hot mixed asphaltic concrete (HMAC).
5. Determine polymer impact on the low and high temperature performance of binders. .
6. Investigate the relation between binder morphology and the physical properties of modified asphalts.
7. Study the viscoelastic behavior of asphalts and asphalts modified by selected polymers of elastomeric and plastomeric types in wide range of temperatures and frequencies.

8. Evaluate the effect of polymers on the properties of asphalt, and compare these properties with those of unmodified asphalt.

CHAPTER 4

Materials and Methods

4.1 Selection of Materials

4.1.1 Selection of Asphalt

The softer asphalt from Husky Oil production (200/300 pen grade) was chosen as a base asphalt for preparation of polymer/asphalt blends in this study. Using the single asphalt base reduced the amount of variables and made evaluation of results easier.

4.1.2 Selection of Polymers

In this thesis, five polymers were chosen to blend with the base asphalt. The selected polymers are listed in Table 3.1.

Table 4.1 Producers and Trade Names for Polymers Selected

MODIFIER TYPE	PRODUCER	TRADE NAME
Styrene / Butadiene / Styrene (SBS)	FINA	Finaprene 411
Styrene / Butadiene / Styrene (SBS)	Shell	Kraton D1102
Styrene / Isoprene / Styrene (SIS)	Shell	Kraton D1107
Ethylene / Vinyl Acetate (EVA)	DuPont	Elvax 150W
Ethylene / Vinyl Acetate (EVA)	DuPont	Elvax 350

4.1.2.1 Structures and Properties of SBS and SIS Polymers

SBS and SIS polymers are a class of elastomers which can be used without vulcanization. The polymers consist of block segments of styrene monomer units and

rubber monomer units. The most common structure is the linear A-B-A block type (styrene-rubber-styrene). Other possible structures include the radial $(A-B)_n$ types (styrene-rubber)_n. In the compositions of the SBS and SIS polymers, the polystyrene blocks form hard domains within the elastomer matrix and act as “physical crosslinkers” between them. During the processing, in the presence of heat and shear or solvent, the polystyrene domains soften and permit flow. After cooling or solvent evaporation, the polystyrene domains reform and harden, locking the polymer network in place again. The physical crosslinking and reinforcing effect gives the SBS and SIS polymers their high tensile strength while the elastomer blocks give the SBS and SIS polymers their elasticities. Since the physical crosslinking is reversible, the scrap SBS and SIS polymers may be recycled. The SBS and SIS consist of block polymers in which the elastomeric portion of the molecule is an unsaturated polymer – either butadiene or isoprene, which improves the low temperature toughness of the plastics, and they also have sufficient compatibility to obtain the uniform, fine polymer dispersion. The details are discussed in following sections:

4.1.2.1.1 Finaprene 411

The Finaprene polymer is manufactured by Fina Chemical Co.. Finaprene 411 is a polystyrene-polybutadiene thermoplastic tribloc radial copolymer. Neither vulcanization nor additive for cross-linking is required because of its high molecular weight. The physical appearance of Finaprene 411 is a relatively rigid white crumb or powder. The properties of the Finaprene 411 are listed in Table 2.

Table 4.2 Properties of Finaprene 411

Butadiene/Styrene Ratio	70/30
Block PS%	30
Typical MW, 10 ³	280
Spec. Gravity, kg/m ³	0.94
Tensile Strength, MPa	23
Elongation at Break, %	670
300% Modulus, MPa	3.3
Hardness, Shore A	80

4.1.2.1.2 Kraton D1102

The Kraton polymer is manufactured by Shell Chemical Co.. Kraton®. Among the Kraton polymers, Kraton 1102 is a triblock copolymer of styrene with a butadiene midblock resulting in the SBS type linear block structure. Kraton D1102 has the smallest styrene block, and it is the easiest polymer to process. Kraton D1102 has low molecular weight tend to give the best results of resistance at low and high temperatures, due to its ability to form a fine dispersion. The low levels of Kraton D1102 can significantly improve the impact strength with only a slight loss in the stiffness, while at high levels, a “super tough” material can be obtained. The detailed properties of the Kraton 1102 are presented in Table 3.3.

Table 4.3 - Properties of Kraton D1102

Tensile Strength, MPa	32
300% Modulus, MPa	2.8
Elongation, %	880
Set at Break, %	10
Hardness, Shore A	71
Specific Gravity, kg/m ³	0.94
Glass Transition Temperature of Rubber Block, °C	-80
Brookfield Viscosity (Toluene Solution) Pa.s at 25 °C	120
Relative MW	Medium/Low
Melt Viscosity, Melt Index, Condition G, gms/10min	6
Styrene/Butadiene Ratio	28/72
Physical Form	Pellet, Powder

4.1.2.1.3 Kraton D1107

Kraton D1107 is the commercial name of a linear styrene-isoprene-styrene block copolymer produced by Shell Chemical Co.. The properties of the Kraton D1107 are listed in Table 3.4.

Table 4.4 - Properties of Kraton D1107

Tensile Strength, MPa	22
300% Modulus, MPa	0.7
Elongation, %	1300
Set at Break, %	10
Hardness, Shore A	37
Specific Gravity, kg/m ³	0.92
Brookfield Viscosity (Toluene Solution), Pa.s at 25 °C	145
Melt Viscosity, Melt Index, Condition G, gms/10min	11
Styrene/Isoprene Ratio	14/86
Physical Form	Pellet

4.1.2.2 Structures and Properties of EVA Polymers

EVA copolymers are thermoplastic materials whose composition, structure and molecular weight can be varied during manufacturing to produce a wide range of commercial grades. No chemical cross-linking between the copolymer molecules occurs. The effectiveness of EVA copolymers as asphalt modifiers are dominated by their molecular weight and vinyl acetate (VA) content. However, the molecular weight of EVA polymers is extremely difficult to measure accurately, and thus it is a standard practice to quote values of Melt Index (MI) instead of molecular weight.

The Melt Index (MI) is an indicator of the molecular weight (MW) and viscosity of the polymer. The MI is measured by the grams of polymer that come out of a narrow orifice held at 190 °C (374 °F) pressed out by specified weight. If the MI is high, the MW and viscosity are low. If the MI is low, the MW and viscosity will be high, and the blends will have benign physical properties such as good heat resistance which can be seen in the high softening point (Ring and Ball) numbers.

The vinyl acetate content controls the degree of crystallinity of the pure copolymer and this has a direct effect upon the properties of the copolymer relevant to binder modification. When the polymer with vinyl acetate concentration greater than

30% is used, such as Elvax 150W, it offers excellent adhesion to nonporous surfaces, broader compatibility with tackifier resins, and greater solubility in organic solvents. Due to the high VA content, the polymers have low crystallinity and are relatively polar. Combined with a high molecular weight (low MI), the polymers are almost “rubbery” in nature, and of good heat resistance.

EVA copolymers can be easily dispersed in, and have a wide compatibility with generally available asphalts. They are also thermally stable at normal mixing and handling temperatures. When incorporated in even small concentrations, they produce considerable improvement in resistance to flow without making the binder too viscous at normal mixing temperatures or adversely affecting laying and compactions characteristics, and without detriment to low temperature properties.

4.1.2.2.1 Elvax 150W and Elvax 350

Elvax 150W and Elvax 350 are manufactured by E. I. DuPont DeNemours and Co.. Elvax is a copolymer of ethylene and vinyl acetate. The physical form of Elvax 150W and Elvax 350 is a relatively rigid white bead. The properties of the Elvax 150W and Elvax 350 are listed in Table 3.5.

Table 4.5 Properties of Elvax 150W and Elvax 350

	Elvax 150W	Elvax 350
Melt Index, g/min	4.3	1.9
Vinyl Acetate, W%	33	25
Density @ 23 °C, kg/m ³	957	948
Tensile Strength, MPa	6.9 - 8.3	14
Elongation at Break, %	900 - 1100	800 - 1000
Elastic (Tensile) Modulus, MPa	10	25
Hardness, Shore A - 2 Durometer, 10 sec	65	80
Softening Point Ring & Ball, °C	110	132

4.2 Preparation of Materials

Polymer modified asphalt (PMA) binders were prepared by blending soft paving asphalt 200/300 pen grade with the selected polymers in three different concentrations 3%, 5% and 7%.

The detailed procedure of PMA mixing is as follows:

1. Weigh the asphalt sample, and calculate the amount of the selected polymer.
2. Stir hot asphalt over hot-plate with a high shear mixer set at low speed.
3. Start to add the polymer into hot asphalt while the temperature is up to 160 °C. When the temperature reaches 180 °C, maintain it for one hour and mix sample at 30 Hz.
4. Stop mixer and the heat controller, take the sample out, separate the sample into cans of different size for easy sampling.

Some difficulties were met when mixing some of 7% of polymers with the asphalt, and these were overcome by applying longer mixing times at 180 °C (about two hours).

4.3 Physical and Empirical Methods Applied for Asphalt Testing

The behavior of asphalt should be explained by its chemical composition and structure. However, the chemical complexity of asphalt makes it very difficult to use chemical analyses to characterize its performance. For this reason, physical property measurements become the primary means in the performance evaluation and selection of asphalt.

The tests used in this thesis are divided into three parts: empirical tests, tests using SUPERPAVE™ specification and rheological tests. They are described in the following sections for both regular asphalt and PMA.

4.3.1 Microscopy of Polymer/Asphalt Blends

Asphalt binders present a unique challenge for microscopic analysis because of their pliable and “sticky” nature. The microscopy measurements were carried out on a Zeiss MC80 Microscope Camera on Axioskop microscope. Standard squashed slides of the polymer/asphalt blends were prepared and viewed under the microscope at room temperature. The 35mm film cassette Mot accepts normal 35mm film 135. The projection lens were used to shoot photographs of various representative sections of the slides. The magnification is either 10× or 40×.

4.3.2 Penetration

The penetration test is an empirical test which measures binder consistency at intermediate service temperatures. The penetration is the distance in tenths of millimeter which a standard needle penetrates into the sample under given conditions of loading, time and temperature which at 25 °C are taken as 100g, 5 seconds. The value of the penetration depends on hardness or softness of the binders. The higher the value, the softer the binder is. This value is also used to indicate the temperature susceptibility parameter e.g. penetration-viscosity number (PVN). The detailed procedure of test is described in ASTM Designation D 5 - 95.

4.3.3 Softening Point (Ring and Ball)

This test is also an empirical test which determines the temperature at which the phase change occurs, in the binder. The test measures the temperature at which the binder can not support the weight of a metal ball and begins to flow. The detailed procedure of the test is described in ASTM Designation D 2398.

4.3.4 Viscosity Measurement by Capillary Viscometer

The test method is used to determine the kinematic viscosity of asphalt binders in order to determine its processability during the production and use of paving mixes.

Kinematic viscosity is the ratio of the viscosity to the density of a liquid. A capillary viscometer is used to measure the flow of a liquid under gravity. The test is carried out usually at 135 °C. In this test, the time in seconds required for the binder to flow under gravity between two timing marks is measured. The results are reported in mm²/s. The detailed test procedure is presented in ASTM Designation D 2170.

4.3.5 Ductility

The ductility of asphalt binders is considered as an indirect measurement of tensile properties of the material. This test measures the distance in centimeters to which the specimen can be elongated before breaking when two ends of a briquette specimen of the material are pulled apart at a specified temperature and speed.

In this test, the sample is melted and poured into a brass mold and allowed to cool at the room temperature, then the mold is put into a water bath at specified temperature. This test is most commonly performed at 25 °C. Samples are maintained at 25 °C by circulating water through the ductility bath during testing. The two ends of the test specimen are pulled apart at the speed of 5 cm/min. The detailed test procedure is described in ASTM Designation D 113.

4.3.6 Data Analysis

1. Temperature susceptibility:
 - Penetration – viscosity number, (PVN) (McLeod, 1968)
2. Durability indicators (Aging Methods):
 - Penetration ratio (25 °C)
 - Viscosity ratio (60 °C)

4.3.6.1 Temperature Susceptibility Parameters

Temperature susceptibility is a measure of the rate with which the consistency of an asphalt material changes with temperature. The temperature susceptibility is often expressed by using empirical parameters. One well known temperature susceptibility parameter is the penetration-viscosity number (PVN).

4.3.6.1.1 Penetration Viscosity Number (PVN)

The penetration viscosity number (PVN) was developed by McLeod (1968) when Penetration Index (PI) failed to provide a good correlation to observed pavement cracking at low temperatures in Canada. It can be measured by two methods: the first one is based on the test of viscosity at 60 °C and penetration at 25 °C. It is defined by the following equation:

$$PVN_{60} = \left[\frac{6.489 - 1.590 \log(Pen_{25}) - \log(\eta_{60})}{1.050 - 0.2234 \log(Pen_{25})} \right] (-1.5) \quad (4.1)$$

where:

PVN_{60} = penetration-viscosity number calculated from penetration at 25 °C and viscosity at 60 °C,

Pen_{25} = penetration at 25 °C, 0.1 mm, and

η_{60} = coefficient of viscosity at 60 °C (mm/s).

The second method is based on the test of viscosity at 135 °C. PVN can be calculated by using the following relationship:

$$PVN_{135} = \left[\frac{4.258 - 0.7967 \log(Pen_{25}) - \log(\eta_{135})}{0.7951 - 0.1858 \log(Pen_{25})} \right] (-1.5) \quad (4.2)$$

where:

PVN_{135} = penetration-viscosity number calculated from penetration at 25 °C, 0.1 mm, and

η_{135} = coefficient of kinematic viscosity at 135 °C (mm/s).

PVN parameter is usually calculated because it is believed to correlate to low temperature performance of HMA pavements.

4.3.6.2 Durability Indicators (Aging Methods)

4.3.6.2.1 Penetration Ratio and Aging Index (Viscosity Ratio)

Penetration ratio and aging index (viscosity ratio) are the ratios of the measured property after aging in the rolling thin film oven test (RTFOT) and thin film oven test (TFOT) to the property before aging.

4.4 SUPERPAVE™ Specification Applied for Asphalt Testing

4.4.1 Flash Point

The flash point of asphalt binder is the temperature at which the vapor pressure is sufficiently high to produce enough hydrocarbon vapors to form an explosive mixture with air when contacted with an open flame. The flash point is an important empirical test; it indicates the safe temperature to which asphalt binder can be heated during its processing, either in mixing plants or in roofing applications.

The apparatus to determine the flash point of asphaltic materials is Cleveland Open Cup that determines the flash and fire point of the binders except those which have

flash point below 79 °C. At the beginning of the test, one has to adjust electric heater so that the rate of temperature increase is 15 °C/min. When the temperature is about 55 °C below the flash point, the rate of temperature increase is lowered to 5 °C/min. The test flame is passed across the cup when the temperature is about 30 °C under the flash point and this continues until a flash appears on the surface of the sample. The flash point is obtained by using the following equation:

$$T = C + 0.03 (760 - P) \quad (4.3)$$

Where T is the flash point temperature (°C),

C is the temperature obtained from the test (°C), and

P is the air pressure at the testing time (mmHg).

The more detailed flash point test procedure can be found in ASTM Designation D 92.

4.4.2 Viscosity in Rotational Viscometer

This viscosity test is used to determine the flow characteristics of the asphalt binder to provide some assurance that it can be handled and pumped during the hot mixing. According to the SHRP specification, the viscosity is measured at 135 °C.

The rotational viscometers are rotating spindle-type viscometers. After pouring the preheated binder into the chamber, the spindle is placed into the sample and attached to the rotating shaft. Thirty minutes are used for the sample to reach the test temperature. During the test, the spindle is rotated by a motor, and the torque necessary to rotate the spindle is measured. Mettler RM 260 and Contraves RM 115 viscometers were used for the measurement of viscosity at 60 °C and 135 °C, respectively.

4.4.3 Rolling Thin Film Oven Test (RTFOT)

This test was developed by the California Highway Department to simulate aging

that occurs during the hot mix and construction of the asphalt concrete. In this test, samples of about 35g of binders are placed in eight open-mouth jars and the jars are placed on their sides in a rotating carriage inside an oven. A moving film of asphalt binders is heated in the oven for 85 minutes at 163 °C. A current of air is periodically blown across the film surface when the jars rotate. At the end of 85 minutes, the jars are removed and aged binder is drained into a suitable size container. The combined effects of heat and air cause oxidative aging of the asphalt. The RTFOT-aged binder is then used for Pressure Aging Vessel (PAV) test and the Dynamic Shear Rheometer (DSR) tests.

The parameter, mass loss, is measured from the sample mass before and after the RTFOT. The mass loss calculated as follows:

$$\text{Mass Loss \%} = [(\text{Original Mass} - \text{Aged Mass}) / \text{Original Mass}] \times 100 \quad (4.4)$$

This detailed test procedure is described in ASTM Designation D 2872

4.4.4 Pressure Aging Vessel (PAV)

The Pressure Aging Vessel (PAV) is used to simulate the physical and chemical property changes that occur in asphalt binders as a result of long-term, in-service oxidative aging in the field.

The PAV measurement using the RTFOT-aged binder, is run under 2.07 MPa air pressure for the standard period of time, 20 hours. The temperature of the test is varied depending on the climate at which the asphalt will be used (asphalt binder grade). The temperature, 90 °C, 100 °C, and 110 °C is required to represent the conditions ranging from cold to hot areas. Ten RTFO-aged binder can be aged in the same vessel with 50g of each binder in a separate pan.

The PAV test is a conditioning test that requires no response recording. However, the temperature and pressure need to be monitored throughout the test. The vessel was removed from the oven after 20 hours, and then weighed samples when the samples are cool. The weight gain is obtained due to oxidation of the binders, and the sample is collected for Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR) tests. The detailed test procedure is detailed in AASHTO PP1.

4.4.5 Bending Beam Rheometer (BBR)

The test in BBR can evaluate the properties of asphalt binders at low pavement temperature (Bahia, et al., 1992). BBR test is used to measure how much a binder creeps or deflects under a constant load at a constant temperature at 1 hour time. The measurement is performed at temperature 10 °C higher than the pavement temperature. According to the time-temperature superposition, SHRP researches confirmed that by raising the test temperature 10 °C, an equal creep stiffness can be obtained after only a 60 second loading. The obvious benefit is that a test result can be measured in a much shorter testing time. There are two values to be measured from BBR. One is the creep stiffness (S) which represents the binder resistance to a constant loading, and the other one is the m-value which represents the asphalt stiffness changes as loads are applied. Current SHRP Binder Specifications for grading the minimum pavement design temperature is based on creep stiffness, and it requires that the S value does not exceed 300MPa at the 60 seconds test time and that the m-value exceeds 0.300. These specifications are used for grading Pressure Aging Vessel (PAV) aged asphalt binders. Anderson (1990) stated that the BBR is the best choice for determining the low-temperature properties of binders.

The BBR consists of an Linear Variable Differential Transformer (LVDT), loading mechanism, temperature bath, and appropriate controls. The sample, loading mechanism, and LVDT are submerged in a constant temperature ethanol bath prior to, and during testing.

The actual test is performed under the load of 980mN for a total time of 240s. A constant load is applied at the center of a 6.25mm*12.5mm*125mm binder beam. The deflection of the beam is measured continuously during loading and software program calculates the flexural creep stiffness, $S(t)$, and the m -value at frequent time intervals.

Unlike the classical test methods, the bending beam geometry is well-defined by elastic beam theory. Using the following equation:

$$S(t) = PL^3 / 4 bh^3 \delta(t) \quad (4.5)$$

where $S(t)$ is the time-dependent creep stiffness (MPa) measured after a constant load (P) is applied, and the deflection $\delta(t)$ is measured over a period of 240 seconds for a rectangular beam having a defined span length (L), width (b) and depth (h). Performing the test up to strains of 1% maintains the response in the linear-viscoelastic region. The detailed test procedure is given in AASHTO PP1.

4.4.6 Dynamic Shear Rheometer (DSR)

The intermediate-temperature and the high-temperature rheological properties were tested in a Bohlin (CS) Rheometer with a parallel plate configuration; one plate is fixed and the other plate oscillates. This instrument is a controlled stress mode apparatus. The binder samples are placed in between two 25mm parallel plates and the gap is adjusted to 1mm for the original and RTFOT binders with high testing temperature range from 46 °C to 82 °C, and strain value set at 2 to 12%. Alternatively, the binder samples are placed in between two 8mm parallel plates, and the gap is adjusted to 2mm for the PAV aged binders with intermediate testing temperature range from 4 °C to 40 °C, and the strain value set about 1%.

Parameters measured by Bohlin (CS) Rheometer are $|G^*|$ (absolute value of the

complex shear modulus) and δ (phase angle). $|G^*|$ measures the total resistance of a material, and it consists of two components: elastic (recoverable) and viscous (nonrecoverable) parts. δ is an indicator of the relative amounts of recoverable and nonrecoverable deformation.

The binders that meet the SUPERPAVE™ specification in the DSR should have improved their performance by limiting the asphalt contribution towards permanent deformation and fatigue cracking in asphalt pavements. The permanent deformation which is also known as rutting is assumed to be governed by the parameter $|G^*|/\sin\delta$. Therefore in order to minimize rutting, $|G^*|/\sin\delta$ must be greater than or equal to 1.00 kPa for the original asphalt binder and 2.20 kPa for RTFOT (Rolling Thin Film Oven Test) at the maximum pavement temperature at a fixed frequency of 10 rad/sec. High values of $|G^*|$ and low values of δ are considered desirable. Like permanent deformation, the fatigue cracking is also assumed to be governed by $|G^*|$ and $\sin\delta$. The $|G^*|\sin\delta$ is known as the fatigue cracking factor which should be less than 5000 kPa. Low values of $|G^*|$ and $\sin\delta$ are desirable for the resistance of fatigue cracking. Again these values are obtained by the DSR for the pressure aged binders.

4.5 Rheological Tests

The small amplitude oscillation shear tests are probably the most frequently used rheological methods to characterize polymer modified asphalt (Berker, et al., 1988). Most of the dynamic mechanical measurements presented in my work have been accomplished on Bohlin (CS) Rheometer with the plate-plate geometry.

4.5.1 Bohlin (CS) Rheometer

The test procedure for Bohlin (CS) rheometer is as follows:

Before testing, install the 25mm diameter plates while the temperature ranges from 30 °C to 70 °C, set the gap to the 1mm. If the temperature range is 5 °C to 25 °C, one has to change to the 8mm diameter plates, set the gap to the 2mm. Prepare the sample. The sample should be preheated until it becomes fluid, stirred to get rid of the air bubbles and make it homogeneous. A small spoon is used to pour a suitable amount of sample onto the center of the upper long stem parallel plate. The upper long stem plate oscillates and the lower plate is fixed. The sample temperature is controlled by a circulating water bath with temperature control unit (TCU). The compressor provides an air pressure of 3 bar to the air bearings.

The test conditions are as follows. Frequency sweeps are performed from 0.01Hz to 2Hz including 0.01, 0.015, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.15, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, 1.50, 2.00Hz to calculate the storage modulus (G') and loss modulus (G''). The dynamic values are reported in rad/sec where $1 \text{ rad/sec} = 1/2\pi \text{ Hz}$. The test temperature is covered from 5 °C to 70 °C for different polymer modified binders shown as following:

3% Fina 411 modified asphalt binder: 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70 °C.

5% Fina 411 modified asphalt binder: 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70 °C.

3% Kraton 1102 modified asphalt binder: 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70 °C.

5% Kraton 1102 modified asphalt binder: 5, 10, 20, 30, 40, 50, 60, 70 °C.

3% Kraton 1107 modified asphalt binder: 5, 10, 20, 30, 40, 50, 60 °C.

5% Kraton 1107 modified asphalt binder: 5, 10, 20, 30, 40, 50, 60 °C.

3% Elvax 350 modified asphalt binder: 5, 10, 20, 30, 40, 50, 60, 70 °C.

5% Elvax 350 modified asphalt binder: 5, 10, 20, 30, 40, 50, 60, 70 °C.

The binders modified with different types and different concentration of polymer and the base asphalt were examined in this research, these are: 200/300 pen grade asphalt,

binders modified with 3% and 5% radial SBS polymer, Finaprene 411, 3% and 5% linear SBS polymer, Kraton D1102, 3% and 5% SIS polymer, Kraton D1107, 3% and 5% EVA polymer, Elvax 350.

Chapter 5

Analysis of Conventional Test Results for Base and Polymer Modified Asphalts

5.1 Results of Empirical Tests

5.1.1 Penetration at 25 °C

Results of penetration at 25 °C before and after RTFOT aging for unmodified and polymer-modified asphalts are shown in Table 5.1 and are plotted in Fig. 5.1. It has been found that before and after RTFOT aging, the value of penetration at 25 °C for the 200/300 conventional asphalt was significantly higher than the values for the polymer-modified asphalt binders.

Table 5.1 Results of Penetration Test

Composition	Code	Penetration @ 25C, [dmm] 100g/5s	
		Before RTFOT	After RTFOT
200/300 pen grade asphalt	A0	290	146
3% radial SBS (Finaprene 411)	B1	135	84
5% radial SBS (Finaprene 411)	B2	95	65
7% radial SBS (Finaprene 411)	B3	81	63
3% linear SBS (Kraton D1102)	C1	162	100
5% linear SBS (Kraton D1102)	C2	104	65
7% linear SBS (Kraton D1102)	C3	74	54
3% SIS (Kraton D1107)	D1	106	81
5% SIS (Kraton D1107)	D2	103	74
7% SIS (Kraton D1107)	D3	90	71
3% EVA (Elvax 150W)	E1	243	112
5% EVA (Elvax 150W)	E2	187	81
7% EVA (Elvax 150W)	E3	135	72
3% EVA (Elvax 350)	F1	188	104
5% EVA (Elvax 350)	F2	138	80
7% EVA (Elvax 350)	F3	111	61

5.1.1.1 Effects of Polymer Type

The effects of polymer on the penetration at 25 °C of the PMA binders before and after RTFOT aging are presented in Figure 5.1. It is obvious that there is a general trend for the PMA binders to have lower penetration before and after RTFOT aging compared to conventional asphalt. However, the decrease of penetration for the binder modified with SBS polymers is lower than the decrease in original asphalt. Blends with Elvax 150W have the decrease in penetration after RTFOT somewhat higher than original asphalt, blends with Elvax 350 have the decrease of penetration lower than that of original asphalt, however more than blends with SBS polymers.

5.1.1.1.1 Asphalt Modified by SBS Polymers

From Figure 5.1, the values of penetration of the binders modified with (3, 5%) of radial SBS polymer, Finaprene 411, (B1 and B2) are lower than those of binders modified with linear SBS polymer, Kraton D1102, (C1 and C2), both before and after RTFOT. At high concentration (7%) of polymers, the value of penetration of the binder modified with radial SBS polymer, Finaprene 411, (B3) is higher than those of the binder modified with linear SBS polymer, Kraton D1102, both before and after RTFOT. Therefore, when the concentration of polymer is up to 7%, the binder modified with radial SBS polymer is softer than the one with linear SBS. At the low concentration, the binder modified with radial SBS is harder than the binder modified with linear SBS polymer. The higher the concentration of SBS (either radial or linear) is, the lower the value of the penetration is.

In the case of the binder modified with SBS polymer, the effect of molecular weight and chemical composition on the properties is determined by the molecular weight of polystyrene and polybutadiene blocks (Diani and Gargani, 1987). From section 4.1.2.1.1 and 4.1.2.1.2, the ratios of styrene and butadiene of radial and linear SBS are 30/70 and 28/72, respectively. The molecular weight of radial SBS (Finaprene 411) is

high, and the molecular of linear SBS (Kraton D1102) is medium/low. As demonstrated in Figure 5.1, the lower the molecular weight of SBS, the higher the penetration values are.

5.1.1.1.2 Asphalt Modified by SIS Polymer

The binder modified with 3% of SIS polymer, Kraton D1107 (D1) exhibited lowest penetrations at 25 °C before RTFOT. The penetration values decrease slightly with increasing the SIS concentrations (D2 and D3). After RTFOT, the values of penetration of binders modified with SIS (D2 and D3) at higher concentrations, 5, 7%, are higher than those of the binders modified with SBS polymers.

The penetration of the binders modified with SIS polymer, Kraton D1107, did not significantly change with the increase of the concentration, compared with the penetration of the binders modified with SBS and EVA polymers.

5.1.1.1.3 Asphalt Modified by EVA Polymers

The binders modified with EVA polymers, Elvax 150W and Elvax 350, (E1, E2, E3, F1, F2, F3) demonstrated highest penetration at 25 °C among the binders modified with other polymers studied. In contrast, the penetration of the binders modified with EVA decreased dramatically after RTFOT. The penetration decreases with the increase of the EVA concentration.

In the case of EVA-modified asphalt, the effects of constituents in the polymer are more pronounced with lower vinyl acetate contents in the EVA copolymer. From section 4.1.2.2.1, the values of vinyl acetate content of EVA polymers, Elvax 150W and Elvax 350, are 33 and 25, respectively. Elvax 350 contains lower vinyl acetate than Elvax 150W. From the Figure 5.1, the material with lower VA content produced harder

polymer/asphalt blends.

The molecular weight of EVA depends on the value of MI (melt index). From section 4.1.2.2.1, the values of MI of Elvax 150W and Elvax 350 are 4.3 and 1.9 g/min, respectively. The molecular weight (MW) of Elvax 150W is lower than that of Elvax 350. It follows from the Figure 5.1 that the material with higher MW of EVA produced harder polymer/asphalt blends.

5.1.1.2 Effects of Aging

Table 5.2 Results of Penetration Ratio

Composition	Code	Penetration Ratio
200/300 pen grade asphalt	A0	0.5
3% radial SBS (Finaprene 411)	B1	0.62
5% radial SBS (Finaprene 411)	B2	0.68
7% radial SBS (Finaprene 411)	B3	0.78
3% linear SBS (Kraton D1102)	C1	0.62
5% linear SBS (Kraton D1102)	C2	0.63
7% linear SBS (Kraton D1102)	C3	0.73
3% SIS (Kraton D1107)	D1	0.76
5% SIS (Kraton D1107)	D2	0.72
7% SIS (Kraton D1107)	D3	0.79
3% EVA (Elvax 150W)	E1	0.46
5% EVA (Elvax 150W)	E2	0.43
7% EVA (Elvax 150W)	E3	0.53
3% EVA (Elvax 350)	F1	0.55
5% EVA (Elvax 350)	F2	0.58
7% EVA (Elvax 350)	F3	0.55

The results of penetration at 25 °C for the PMA binders indicate that aging by RTFOT may have less effect on penetration values for polymer-modified asphalt binders than on those values for unmodified asphalt. To demonstrate this effect, the penetration ratio after aging by RTFOT for the unmodified and modified asphalt binders was evaluated. These results are shown in Table 5.2, and are plotted in Figure 5.2. The higher the penetration ratio is, the less the effect of aging is. The values of penetration ratio are all less than one because of the oxidative hardening occurred during the RTFOT. One reason of lesser hardening in the case of PMA can be that polymer absorbs the oils so that the loss of volatiles is lower. That would have to be confirmed by mass loss of binders which is shown in Table 6.2.

5.1.1.2.1 Asphalt Modified by SBS Polymers

Figure 5.2 shows that aging by RTFOT has less effect with the increase of the concentration of the radial SBS, Finaprene 411, modified asphalt (A1, A2 and A3). As for the binder modified with the linear SBS, Kraton D1102, aging by RTFOT has almost the same effect when the concentration of Kraton D1102 is 3 and 5%. When the concentration increases to 7%, aging has less effect on the binder modified with the linear SBS, Kraton D1102. The higher the concentration is, the less of aging occurs. The values of penetration ratio of the binder modified with 7% of SBS polymers are close to one, indicating a better resistance to oxidative hardening during plant mixing.

5.1.1.2.2 Asphalt Modified by SIS Polymer

Figure 5.2 shows that aging by RTFOT has the least effect on the binders modified with SIS polymer Kraton D1107, (D1, D2, and D3). The binders modified with Kraton D1107 (D1, D2, D3) have penetration ratios close to one, indicating a better resistance to oxidative hardening during plant mixing.

5.1.1.2.3 Asphalt Modified by EVA Polymers

Figure 5.2 shows that aging by RTFOT has the greatest effect on penetration of the binder modified with EVA polymers, Elvax 150W and Elvax 350, especially on the binder modified with lower concentrations of EVA polymer Elvax 150W (E1 and E2) with low molecular weight and high vinyl acetate content. The binders modified with Elvax 350 (F1, F2) have higher penetration ratios than the binders modified with lower concentrations (3, 5%) of Elvax 150W. The binders modified with high concentration, 7% of Elvax 150W and Elvax 350 (E3, F3), have penetration ratios similar. Therefore, the binders modified with the concentrations up to 5% of Elvax 350, which has high molecular weight and low vinyl acetate content, have better resistance to oxidative hardening during plant mixing than those of Elvax 150W which are with low MW and high VA. Although all of the binders modified with EVA polymers, Elvax 150W and Elvax 350, have poor resistance to oxidative hardening compared with the binders modified with SBS and SIS polymers. As saturated polymers, Elvax 150W and Elvax 350 do not decompose. Therefore, the hardening of the binders modified with EVA polymers, Elvax 150W and Elvax 350 is closer to the base asphalt.

5.2 Softening Point R&B

The experimental values of softening point R&B for unmodified and polymer-modified asphalts are listed in Table 5.3 and shown in Figure 5.3.

Table 5.3 Results of Softening Point R&B

Composition	Code	Softening Point R&B [°C]
		Before RTFOT
200/300 pen grade asphalt	A0	36
3% radial SBS (Finaprene 411)	B1	46
5% radial SBS (Finaprene 411)	B2	54
7% radial SBS (Finaprene 411)	B3	72
3% linear SBS (Kraton D1102)	C1	41
5% linear SBS (Kraton D1102)	C2	52
7% linear SBS (Kraton D1102)	C3	57
3% SIS (Kraton D1107)	D1	45
5% SIS (Kraton D1107)	D2	50
7% SIS (Kraton D1107)	D3	55
3% EVA (Elvax 150W)	E1	38
5% EVA (Elvax 150W)	E2	45
7% EVA (Elvax 150W)	E3	48
3% EVA (Elvax 350)	F1	41
5% EVA (Elvax 350)	F2	49
7% EVA (Elvax 350)	F3	57

5.2.1 Effects of Polymer Type

The values of softening point for the polymer-modified binders (B-F) are all higher than that of the unmodified binder (A0). The values of softening point increases with the increased concentration of polymer.

5.2.1.1 Asphalt Modified by SBS Polymers

Figure 5.3 shows that the values of the softening point of the binders modified with the radial SBS polymer, Finaprene 411, (B1, B2, B3) are significantly higher than those of other polymer-modified binders, especially the binder modified with of 7% Finaprene 411, (B3). Therefore, among all the tested polymer modified binders, the binders modified with higher MW SBS polymer has the greatest effect on softening point of polymer/asphalt blends.

5.2.1.2 Asphalt Modified by SIS Polymer

Figure 5.3 shows that the value of softening point of binder modified with 3% SIS polymer, Kraton D1107, (D1) has increased when compared to the base asphalt (A0). When the concentration of Kraton D1107 is more than 3%, the softening point values of the binders modified with Kraton D1107 (D2 and D3) increase steadily.

5.2.1.3 Asphalt Modified by EVA Polymers

Among the studied polymer modified asphalts, The EVA polymers (E1, E2, E3) demonstrate the least effect on softening point of polymer/asphalt blends when compared to other polymers, especially at high concentration of polymer, 7%, (E3 (=48) < D3 (=55) < F3, C3 (=57) < B3 (=72), however, they are still considerably higher than base asphalt. The values of softening point of binders modified with Elvax 350 (F1, F2, and F3) increase steadily with the increasing of the concentration of the polymer, and they are all higher than those of the binders modified with Elvax 150W (E1, E2, and E3). The softening point of binder modified with 7% Elvax 350 (F3=57) is as high as that of the binder modified with the linear SBS polymer, Kraton 1102, (C3=57). Therefore, the binder modified with high concentration of EVA polymer, Elvax 350, with high molecular weight and low VA has same value of the softening point as polymer/asphalt blends with low MW of SBS polymer, Kraton D1102.

5.3 Viscosity at 60 °C

The average values of viscosity at 60 °C before and after RTFOT aging are presented in Table 5.4 and plotted in Figure 5.4. All binders modified with polymers (B-F) are significantly more viscous than the unmodified asphalt (A0) both before and after RTFOT aging. An increase in viscosity of the binders at a high pavement temperature usually means a higher resistance to rutting of the pavement (Zanzotto, 1987). The viscosity value of the polymer modified asphalt at 60 °C is of specific importance as it controls the deformation of asphalt surface at which it is often considered the highest pavement temperature.

Table 5.4 Results of Viscosity at 60 °C

Composition	Code	Viscosity @ 60 °C (Shear Rate 0.07s ⁻¹) [Pa.s]	
		Before RTFOT	After RTFOT
200/300 pen grade asphalt	A0	48.6	106
3% radial SBS (Finaprene 411)	B1	243	573
5% radial SBS (Finaprene 411)	B2	814	1360
7% radial SBS (Finaprene 411)	B3	4850	Too high to test
3% linear SBS (Kraton D1102)	C1	93	316
5% linear SBS (Kraton D1102)	C2	358	995
7% linear SBS (Kraton D1102)	C3	761	2050
3% SIS (Kraton D1107)	D1	194	418
5% SIS (Kraton D1107)	D2	265	593
7% SIS (Kraton D1107)	D3	562	1210
3% EVA (Elvax 150W)	E1	119	314
5% EVA (Elvax 150W)	E2	154	325
7% EVA (Elvax 150W)	E3	177	380
3% EVA (Elvax 350)	F1	137	398
5% EVA (Elvax 350)	F2	175	438
7% EVA (Elvax 350)	F3	256	495

5.3.1 Effects of Polymer Type

As shown in Figure 5.4, all the polymer-modified asphalt binders (B-F) showed increase in viscosity at 60 °C. This trend occurs both before as well as after RTFOT aging.

5.3.1.1 Asphalt Modified by SBS Polymers

It is shown in Figure 5.4 that the increase of the viscosity of binder, modified with radial SBS polymer Finaprene 411 (B3) is considerable, especially at the concentration of 7%. As for the binders modified with the linear SBS polymer, Kraton D1102, (C1, C2, and C3), the viscosity also significantly increases with the increasing of the concentration of the polymer. Although the viscosity of the binder modified with the high concentration of radial SBS polymer, Finaprene 411, is really high, it is not reasonable to be used for pavement. The binders modified with the linear SBS and the radial SBS polymers, Kraton D1102 and Finaprene 411, respectively, in low concentration should have good resistance against rutting of the pavement.

5.3.1.2 Asphalt Modified by SIS Polymer

The viscosities of binders with Kraton D1107 (D1, D2, and D3) significantly increase with the increasing the concentration of the polymer, although they do not reach the levels achieved in binders modified with SBS polymers, Finaprene 411 and Kraton D1102. When the concentration of Kraton D1107 is 7%, the viscosity almost doubles relative to the viscosity of asphalt modified with 3% of this polymer. Binders modified with Kraton D1107 should contribute to the pavement rutting resistance.

5.3.1.3 Asphalt Modified by EVA Polymers

As can be seen on the Figure 5.4, the EVA polymers (E1, E2, E3, F1, F2, F3) have the least effect on viscosity of asphalt binders when compared with other polymers, although the viscosities of EVA/asphalt blends are still higher than the viscosity of the base asphalt. The viscosities of the binders modified with EVA polymers, Elvax 150W and Elvax 350 do not increase significantly with the increased concentration of the polymers. The viscosities of the binders modified with EVA polymer, Elvax 350, with high molecular weight and low VA (F1, F2, and F3) are somewhat higher than those of the binders modified with EVA polymer, Elvax 150W, with low molecular weight and high VA (E1, E2, and E3). The binders modified with EVA polymer, Elvax 350, with high molecular weight and low VA should provide better resistance to rutting of pavement than binders modified with Elvax 150W.

5.3.2 Effects of Aging

The viscosity ratio is defined as the ratio of the viscosity of the binder after aging to the viscosity of the binder before aging. This ratio is often referred as aging index. A higher value of viscosity ratio indicates a higher degree of age hardening. The values of viscosity ratio of RTFOT-aged binders at 60 °C are given in Table 5.5 and plotted in Figure 5.5. The current ASTM specifications for viscosity graded asphalts specify that the viscosity ratio after RTFOT must be less than five (ASTM, 1990). The RTFOT-aged binders studied in my thesis all meet this requirement (Fig. 5.5).

Table 5.5 Results of Aging Index

Composition	Code	Aging Index (Viscosity Ratio)
200/300 pen grade asphalt	A0	2.18
3% radial SBS (Finaprene 411)	B1	2.36
5% radial SBS (Finaprene 411)	B2	1.67
7% radial SBS (Finaprene 411)	B3	too high to test
3% linear SBS (Kraton D1102)	C1	3.4
5% linear SBS (Kraton D1102)	C2	2.78
7% linear SBS (Kraton D1102)	C3	2.69
3% SIS (Kraton D1107)	D1	2.15
5% SIS (Kraton D1107)	D2	2.24
7% SIS (Kraton D1107)	D3	2.15
3% EVA (Elvax 150W)	E1	2.64
5% EVA (Elvax 150W)	E2	2.11
7% EVA (Elvax 150W)	E3	2.15
3% EVA (Elvax 350)	F1	2.91
5% EVA (Elvax 350)	F2	2.5
7% EVA (Elvax 350)	F3	1.93

5.3.2.1 Asphalt Modified by SBS Polymers

As shown in Figure 5.5, aging by RTFOT has the greatest effect on viscosity ratio of binders modified with the linear SBS polymer, Kraton D1102 (C1, C2, C3), especially the binder modified with low concentration of Kraton D1102. The aging has the least effect on the binder modified with the high concentration of the radial SBS polymer,

Finaprene 411, (B2). The viscosity of 7% of radial SBS binder is too high to be tested since it is beyond the range of the used rheometer. The binders modified with the linear SBS polymer, Kraton D1102, have higher degree of age hardening than the binders modified with the other polymers. On the contrary, the binder modified with 5% of the radial SBS polymer, Finaprene 411, has lower degree of age hardening than the base asphalt and other binders modified with polymers.

5.3.2.2 Asphalt Modified by SIS Polymer

It is observed that the viscosity ratios of the binders modified with SIS polymer, Kraton D1107, (D1, D2, and D3) change very little in spite of the increasing of the concentration of the polymer. The viscosity ratios of binders modified with 3 and 5% of Kraton D1107 are almost as same as the viscosity ratio of the base asphalt. Therefore, adding the SIS polymer, Kraton D1107, into the asphalt, does not have much effect on the age hardening.

5.3.2.3 Asphalt Modified by EVA Polymers

From Figure 5.5, it seems that the viscosity ratio of the binder modified with low concentration of EVA polymer, Elvax 150W, with low molecular weight and high VA, (E1), increases, while it decreases with the increase of concentration of the polymer (E2 and E3). The ratios of E2 and E3 are even lower than that of base asphalt. Same trend is observed in asphalt modified with EVA, Elvax 350, with high molecular weight and low VA (F1, F2, and F3) except that values of F1 and F2 are higher than those of E1 and E2.

5.4 Kinematic Viscosity at 135 °C

The values of kinematic viscosity of base and modified asphalts are shown in Table 5.6 and plotted in Figure 5.6.

Table 5.6 Results of Kinematic Viscosity at 135 °C

Composition	Code	Kinematic Viscosity @ 135 °C (mm ² /s)
		Before RTFOT
200/300 pen grade asphalt	A0	199.6
3% radial SBS (Finaprene 411)	B1	579
5% radial SBS (Finaprene 411)	B2	1457
7% radial SBS (Finaprene 411)	B3	2714
3% linear SBS (Kraton D1102)	C1	437
5% linear SBS (Kraton D1102)	C2	747
7% linear SBS (Kraton D1102)	C3	1194
3% SIS (Kraton D1107)	D1	408
5% SIS (Kraton D1107)	D2	699
7% SIS (Kraton D1107)	D3	1269
3% EVA (Elvax 150W)	E1	362
5% EVA (Elvax 150W)	E2	550
7% EVA (Elvax 150W)	E3	853
3% EVA (Elvax 350)	F1	398
5% EVA (Elvax 350)	F2	634
7% EVA (Elvax 350)	F3	1003

5.5.1 Effects of Polymer Type

From Figure 5.6, it is observed that all the polymer-modified binders (B-F) have higher kinematic viscosity values than unmodified asphalt binder (A0). The higher the polymer concentration is, the higher the kinematic viscosity values are.

5.4.1.1 Asphalt Modified by SBS Polymers

Figure 5.6 shows that the binders modified with the radial SBS, Finaprene 411, (B1, B2, and B3) have dramatically higher kinematic viscosity values compared to the other polymer modified binders. The viscosity of the binder modified with the high concentration of radial SBS polymer, Finaprene 411, is very high, this material, even according to other properties should not be used for paving. The kinematic viscosity values of linear SBS modified binders (C1, C2, and C3) significantly increase with the concentration of polymer, but are much lower than those binders modified with Finaprene 411, especially at higher concentrations. All the tested binders modified with the linear SBS polymer, Kraton D1102 and the binder with the radial SBS polymer, Finaprene 411, except for binder modified with 7% Finaprene 411, should provide improved resistance to rutting of pavement at high temperatures. All tested modified asphalts, except for probably the asphalt modified with 7% Finaprene 411 can be used for the production of paving mixes with the existing equipment.

5.4.1.2 Asphalt Modified by SIS Polymer

The values of kinematic viscosity of the binders modified with the different concentrations of SIS polymer, Kraton D1107, are almost as same as those of the binders modified with the linear SBS polymer, Kraton D1102. The same applies for their processability during mixing and paving operations.

5.4.1.3 Asphalt Modified by EVA Polymers

The binders modified with EVA polymers, Elvax 150W and Elvax 350, have the least effects on the kinematic viscosity as shown in Figure 5.6. However, the values of kinematic viscosity of the binders modified with EVA polymers (E1, E2, E3, F1, F2, and F3) are much higher than that of the base asphalt (A0). EVA polymer, Elvax 350, with high molecular weight and low VA have more effects on binder viscosity (F1, F2, and F3) than EVA, Elvax 150W, with low molecular weight and high VA (E1, E2, and E3), especially at binders with high concentration of polymer. Again, no problems are

expected in processing of these modified asphalts.

5.5 Penetration Viscosity Number (PVN)

Table 5.7 presents the values of PVN for the unmodified and modified asphalt binders. A high value of PVN would indicate a material that has low temperature susceptibility.

Table 5.7 Results of the PVN

Composition	Code	PVN 135	PVN 60
pen 200/300 grade asphalt	A0	0.02	-2.66
3% radial SBS (Finaprene 411)	B1	0.76	-1.87
5% radial SBS (Finaprene 411)	B2	1.69	-1.07
7% radial SBS (Finaprene 411)	B3	2.37	0.56
3% linear SBS (Kraton D1102)	C1	0.56	-2.72
5% linear SBS (Kraton D1102)	C2	0.79	-1.82
7% linear SBS (Kraton D1102)	C3	1.03	-1.51
3% SIS (Kraton D1107)	D1	-0.12	-2.46
5% SIS (Kraton D1107)	D2	0.68	-2.16
7% SIS (Kraton D1107)	D3	1.4	-1.55
3% EVA (Elvax 150W)	E1	0.86	-1.8
5% EVA (Elvax 150W)	E2	1.18	-1.91
7% EVA (Elvax 150W)	E3	1.39	-2.23
3% EVA (Elvax 350)	F1	0.62	-2.04
5% EVA (Elvax 350)	F2	0.94	-2.21
7% EVA (Elvax 350)	F3	1.35	-2.1

It can be seen that most of the modified asphalt binders show significantly higher PVN as compared with the unmodified asphalt, except for 3% linear SBS, SIS and 7%

EVA (Elvax 150W), and the PVN in most cases becomes higher as the concentration of polymer modifier increases. Among all modifiers, the SBS group (either radial or linear) increases the PVN the most. Therefore temperature susceptibility of the polymer modified binders (B-F) is lower than that of unmodified binders, when the penetration viscosity numbers (PVN) are compared. The reduced temperature susceptibility of polymer modified asphalt should provide better resistance to rutting at high service temperatures and better resistance to cracking at low service temperatures.

The shrinkage cracking of asphalt surfaces usually depends on the temperature sensitivity of binder (Jain et al., 1992). Jain et al. also proposed that the measurement of the penetration viscosity number is of considerable significance for selection of polymer as well as determination of polymer concentration. This, however, is somewhat questionable. PVN has limited validity when applied to polymer modified asphalt because the procedure assumes linearity for temperature susceptibility between 25 °C (pen) and 135 °C (kinematic viscosity). For some of the modified binders tested, temperature susceptibility was clearly curvilinear (Figure 5.7) and as a result, PVN results may be misleading.

Other conventional tests I have conducted for polymer modified and unmodified asphalt binders were ductility, flash point, and viscosity at 135 °C. The details of these test results will be not discussed in this thesis.

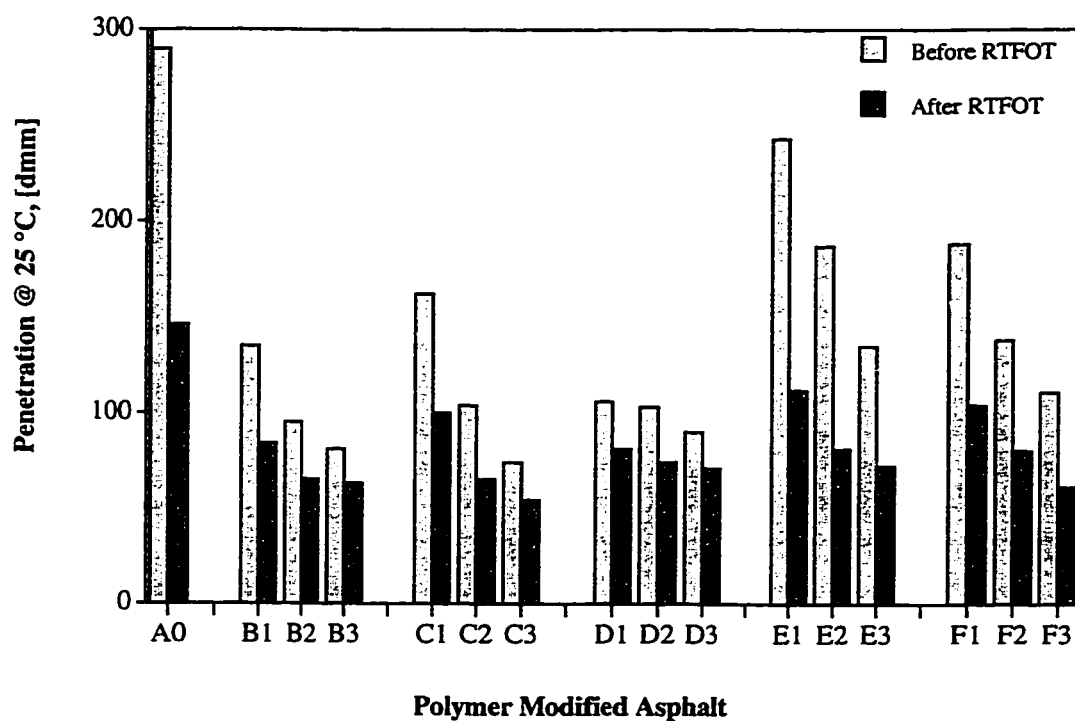


Figure 5.1 Penetration at 25 °C for Unmodified (A0) and Modified Binders (B-F) Before and After RTFOT Aging

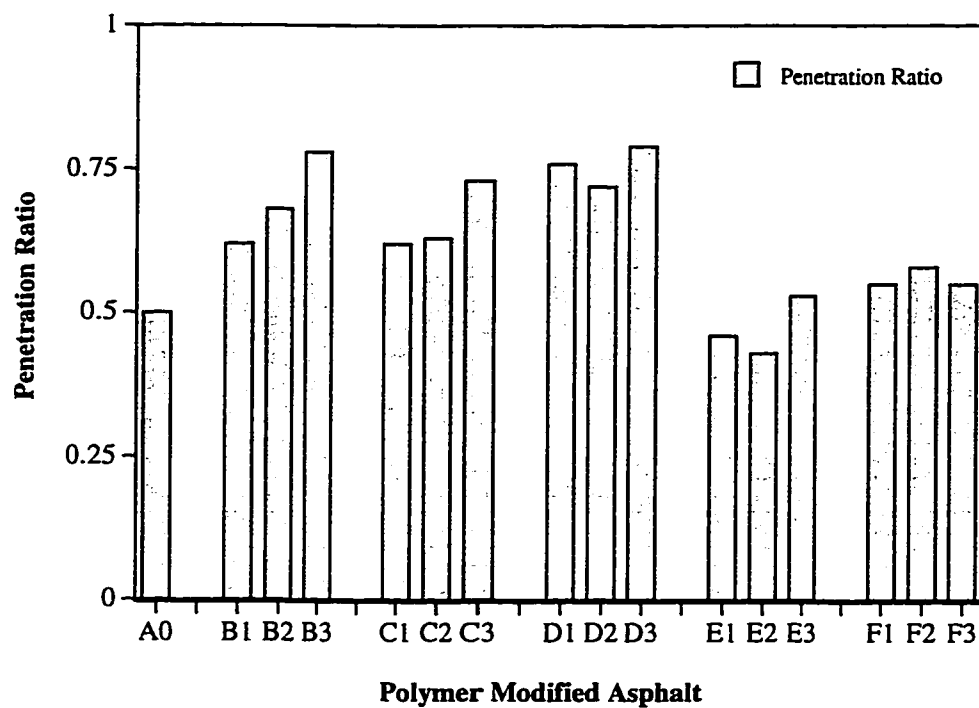


Figure 5.2 Penetration Ration at 25 °C for Unmodified (A0) and Modified Binders (B-F)

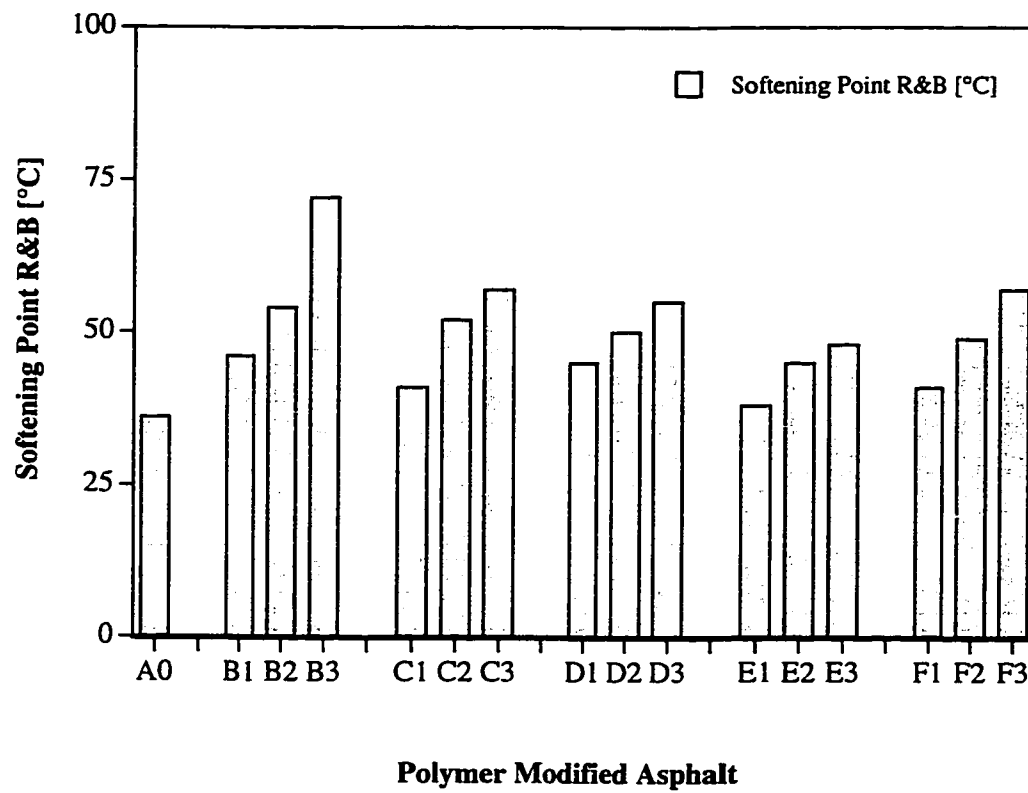


Figure 5.3 Softening Point R&B for Unmodified (A0) and Modified Binders (B-F)

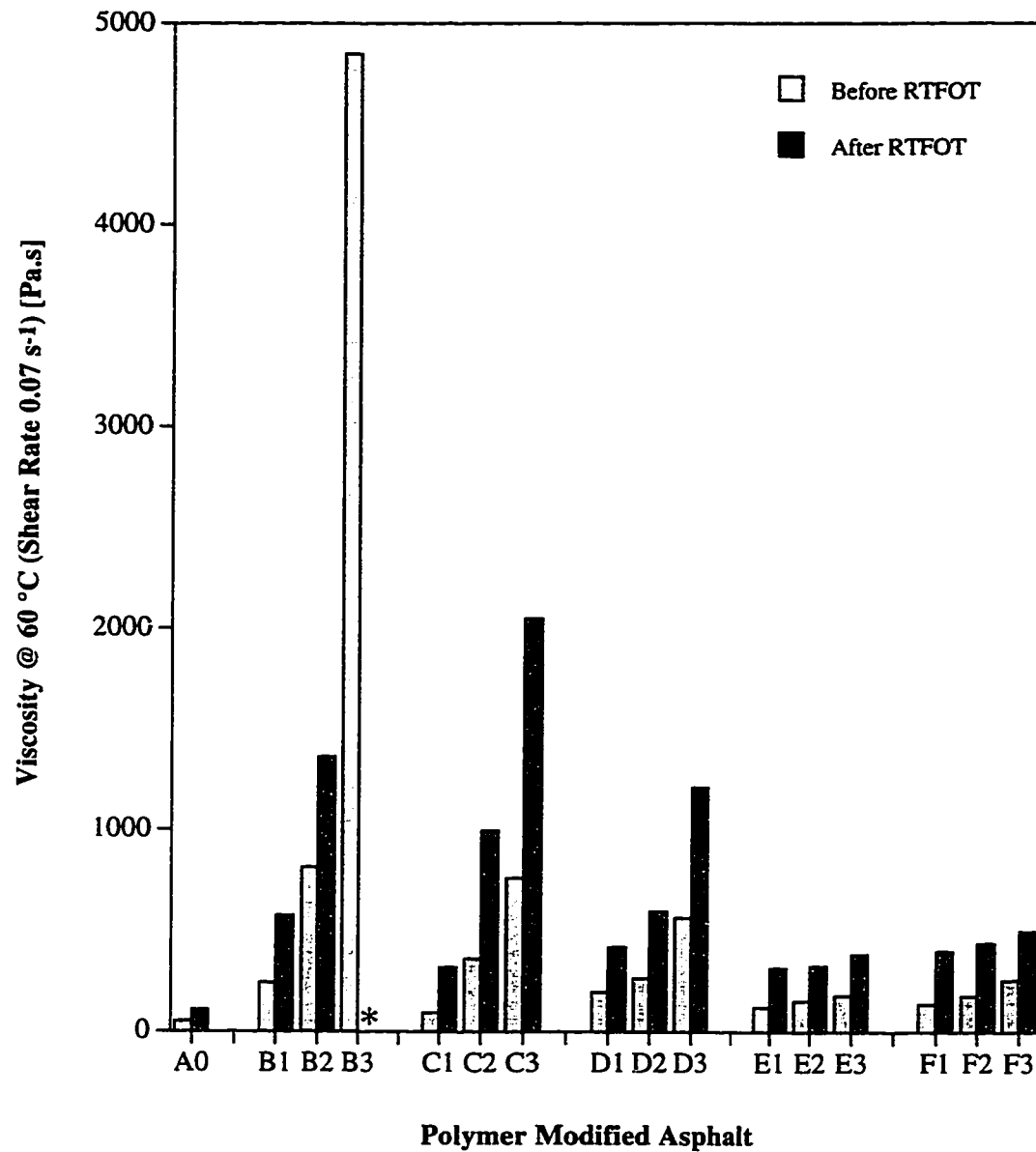


Figure 5.4 Viscosity at 60 °C for Unmodified (A0) and Modified Binders (B-F)
An Asterisk (*) Indicated That the Sample Was Too Viscous to Be Tested

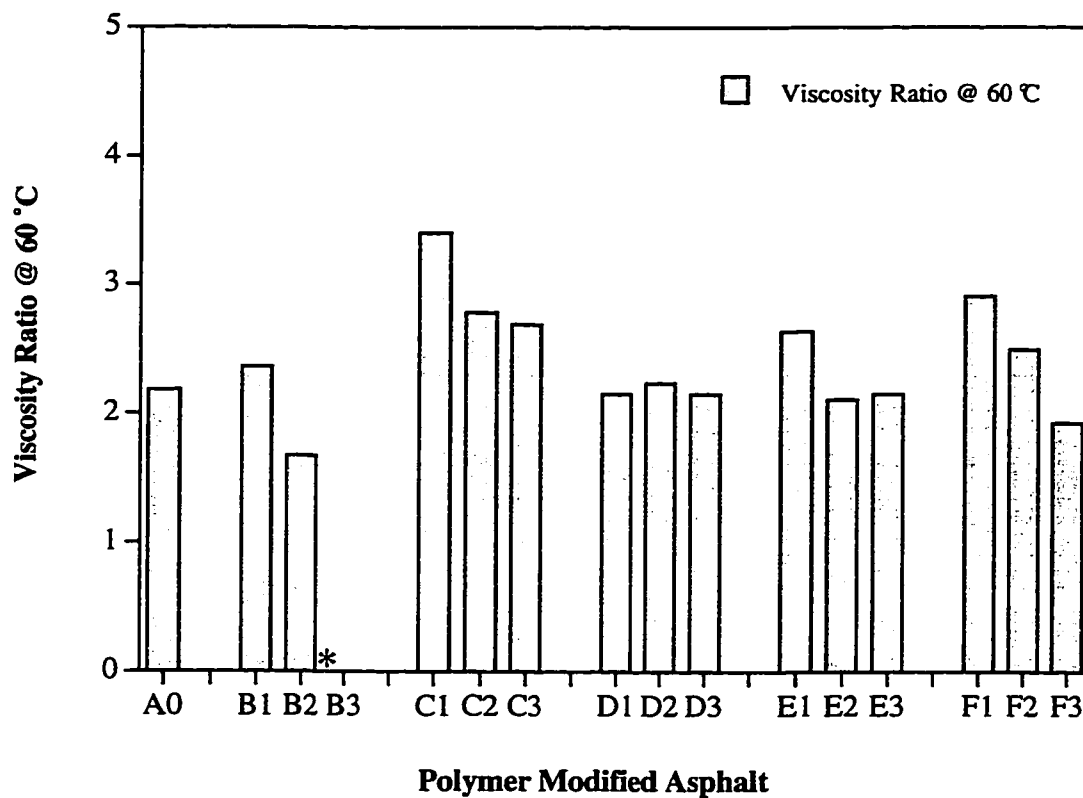


Figure 5.5 Viscosity Ratio at 60 C for Unmodified Asphalt (A0) and Modified Binders (B-F)

An Asterisk (*) Indicated That the Sample Was Too Viscous to Be Tested

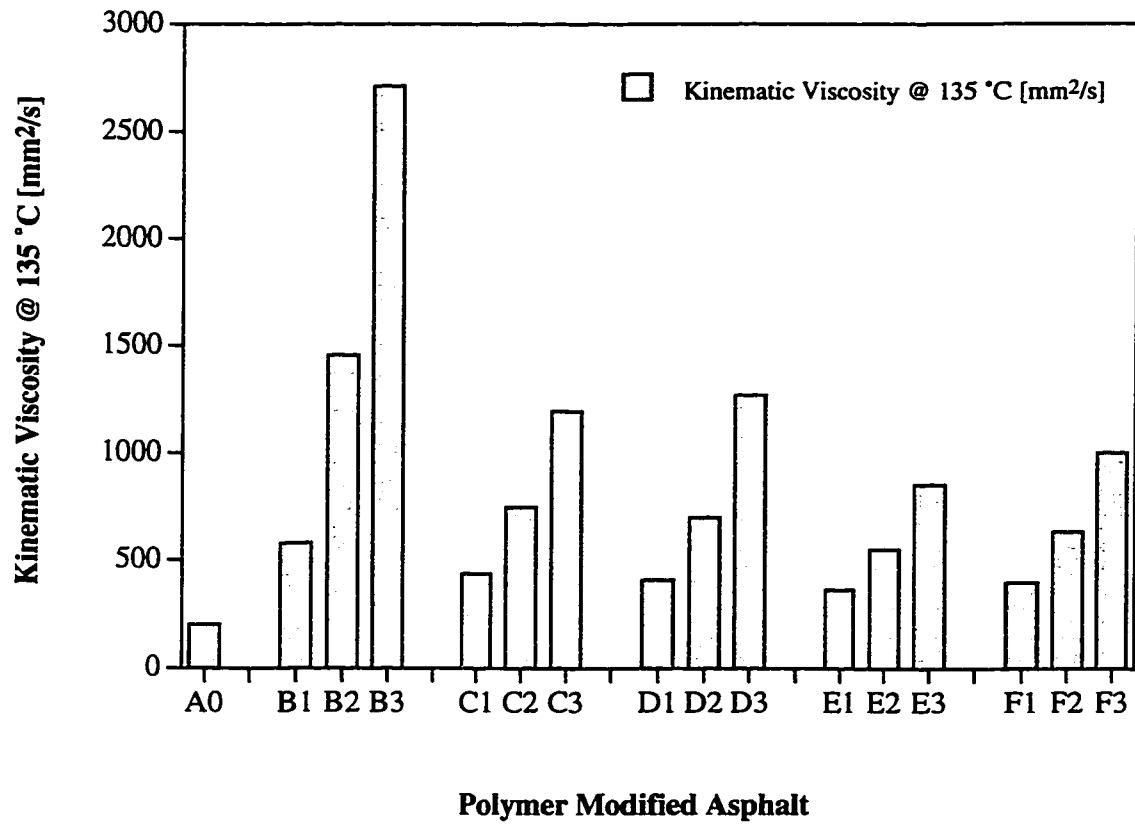


Figure 5.6 Kinematic Viscosity at 135 °C for Unmodified (A0) and Modified Binders (B-F)

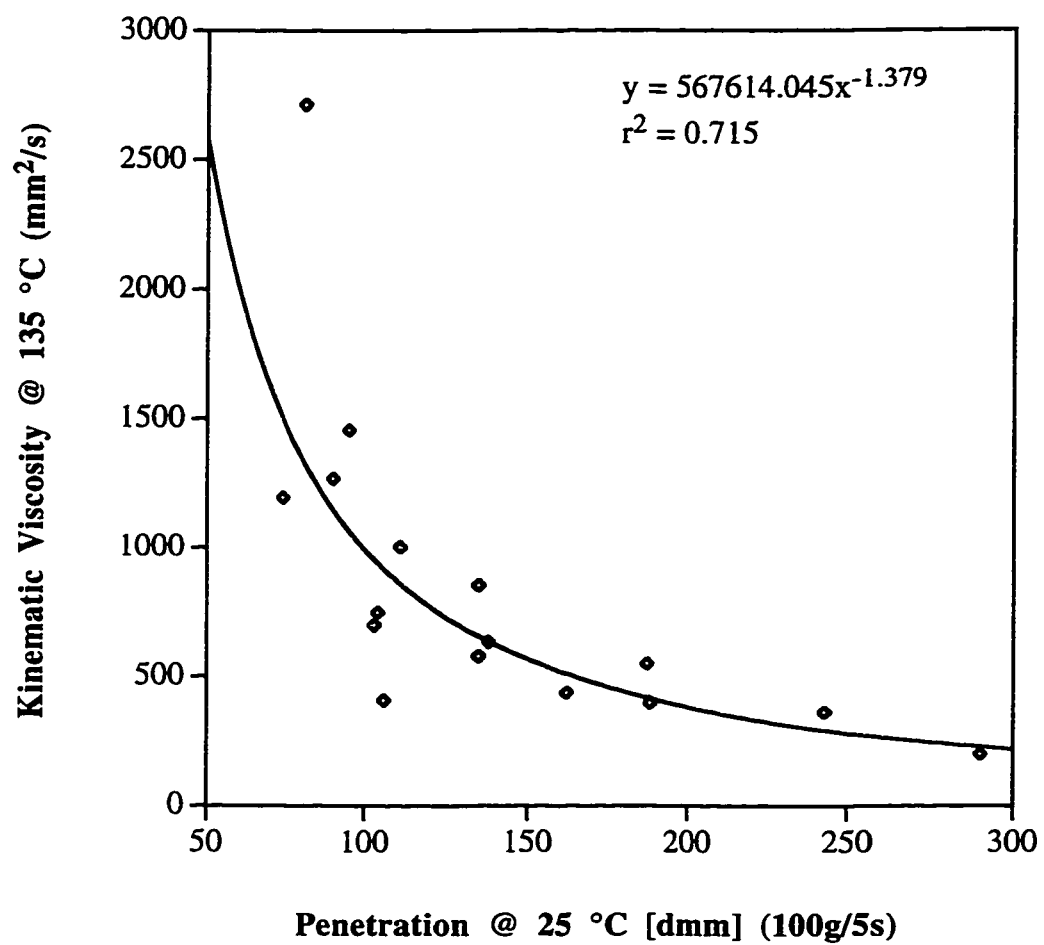


Figure 5.7 Kinematic Viscosity at 135 °C vs. Penetration at 25 °C

Chapter 6

Analysis of SHRP Test Results of Base and Polymer Modified Asphalts

6.1 Effects of Polymers on the High-Temperature Properties of Asphalts

6.1.1 Dynamic Shear Rheometer Test

The details of dynamic shear rheometer test have been discussed in section 4.5.1. According to the SHRP binder specifications, the parameter $|G^*|/\sin \delta$ is an indicator of the rutting resistance for asphalt binders. The permanent deformation of a binder is controlled by $|G^*|/\sin \delta$ on unaged binder (≥ 1.0 kPa), and $|G^*|/\sin \delta$ on RTFOT aged binder (≥ 2.2 kPa). Whichever temperature value is lower (original binder, or binder after RTFOT), this value represents the highest service temperature to which given binder can be exposed. The parameter $|G^*|/\sin \delta$ and the highest service temperatures for the original (unaged) binders and their RTFOT counterparts are presented in Table 6.1.

The relationship between the temperature at which $|G^*|/\sin \delta$ meets the specification requirement and the concentration of the polymer in the polymer/asphalt blend is shown in Figure 6.1 and Figure 6.2. Both figures indicate an increase in this temperature value when the modifiers of SBS, SIS and EVA are mixed with the base asphalt. The effects of the increasing modifier content can be observed in the unaged and RTFOT-aged binders; the temperature value increases as the polymer concentration increases. Particularly, the effects of the radial SBS (Finaprene 411) are the strongest from among all polymers studied (Figure 6.1 and 6.2). The increase of the highest service temperature should give the binders an improved resistance to permanent deformation. All modifiers used in this study are effective in improving the binder properties at high pavement temperatures when the concentration of the polymers is increased.

Table 6.1 Parameter $|G^*|/\sin\delta$ and the Highest Service Temperature for Original (unaged) Binders and the Binders after RTFOT

Composition	Original Binder		RTFOT Binder		T_{high} [°C]
	$G^*/\sin(\delta)$	T_{high}	$G^*/\sin(\delta)$	T_{high}	
	(Min. 1.0 kPa) [kPa]	[°C]	(Min.2.20 kPa) [kPa]	[°C]	
200/300 pen base asphalt	1.02	54	2.53	52	52
3% radial SBS (Finaprene 411)	1.07	68	2.4	63.1	63.1
5% radial SBS (Finaprene 411)	1.03	78.9	2.25	69.9	69.9
7% radial SBS (Finaprene 411)	3.7	79.9	2.48	79	79
3% linear SBS (Kraton D1102)	1.04	60.2	2.39	60	60
5% linear SBS (Kraton D1102)	1.05	69.2	2.33	71	69.2
7% linear SBS (Kraton D1102)	1.09	76	2.26	74	74
3% SIS (Kraton D1107)	1.06	64	2.25	61.1	61.1
5% SIS (Kraton D1107)	1.11	68.8	2.28	65	65
7% SIS (Kraton D1107)	1	73	2.31	69.8	69.8
3% EVA (Elvax 150W)	1.12	57	2.35	58.1	57
5% EVA (Elvax 150W)	1.01	57.9	2.33	62	57.9
7% EVA (Elvax 150W)	1.06	63.1	2.32	63	63
3% EVA (Elvax 350)	1.004	58	2.39	59	58
5% EVA (Elvax 350)	1.02	61.1	2.29	60.9	60.9
7% EVA (Elvax 350)	1.01	66	2.25	65.9	65.9

6.1.1.1 Original Binders (Unaged)

6.1.1.1.2 Asphalt Modified by SBS Polymers

Figure 6.1 shows that the binders modified with the radial SBS polymer, Finaprene 411, have the highest service temperatures at each concentration compared

with other polymers. The binders modified with the linear SBS polymer, Kraton D1102, have the second highest service temperatures if the concentration of the polymer is 5% or more. The binder modification with the radial SBS polymer is the most efficient one in improving the resistance to permanent deformation of binders. The linear SBS polymer also can improve the resistance to permanent deformation, especially in the increased concentration.

6.1.1.1.3 Asphalt Modified by SIS Polymer

The high service temperatures of the binders modified with SIS polymer, Kraton D1107 are higher than the high service temperatures of the binders modified with the linear SBS polymer, Kraton D1102, when the concentration of polymers is lower than 5%. Compared to other polymer modified asphalts, only in the case the binder modified with SIS polymer, the rate of the temperature change decreases when the concentration of the polymer is higher than 3%. With the increasing concentration of the SIS, the ability of its contribution to the pavement resistance to permanent deformation increases more slowly relative to other polymers.

6.1.1.1.4 Asphalt Modified by EVA Polymers

The increase of the high service temperature parameter $|G^*|/\sin \delta$ of binders modified with EVA polymers is lower, than this increase in binders modified with SBS or SIS polymers. When the concentration of EVA increases, the temperature of $|G^*|/\sin \delta$ increases. The high service temperatures of the binders modified with EVA polymer, Elvax 350, with a higher molecular weight and a lower VA are higher than the high service temperatures of the binders modified with EVA polymer, Elvax 150W, with a lower molecular weight and a higher VA. The increase of the rate of the high service temperature is higher when the concentration of Elvax 350 is more than 3%; while the increase of the rate of the high service temperature is higher when the concentration of Elvax 150W is more than 5%. The binders modified with EVA polymers, Elvax 150W

and Elvax 350, have less effect on the improvement of the resistance to permanent deformation compared with the binders modified with SBS and SIS polymers.

6.1.1.2 RTFO-Aged Binders

6.1.1.2.1 Asphalt Modified by SBS Polymers

Figure 6.2 shows that for the RTFO-aged binder, the high service temperature of the binder modified with the radial SBS, Finaprene 411, increases with the increasing of the polymer concentration. The binder modified with the radial SBS has the highest high service temperature compared to the other polymer-modified binders. Therefore, it is the most efficient one for the improvement of resistance to permanent deformation. The high service temperature of the binder modified with the linear SBS, Kraton D1102, increases significantly when the concentration of the polymer is increased from 3% to 5%. However, when the concentration of the linear SBS is more than 5%, the high service temperature increases more slowly. When the polymer concentration is lower than 3%, the high service temperatures of the binder modified with the linear SBS, Kraton D1102 are lower than the high service temperatures of the binder modified with the SIS polymer, Kraton D1107. Therefore, the binder modified with the linear SBS with a concentration ranged from 3% to 5% is more efficient on the improvement of the resistance to permanent deformation after the RTFO-age.

From the figure 6.1 and 6.2, all the high service temperatures of binders modified with the radial SBS polymer, Finaprene 411, after aging, are lower than those of binders before aging, same as the base asphalt. After aging, the ability of the binders modified with Finaprene 411 of the resistance to permanent deformation decreases. Same trend can be seen from the most of the binders modified with linear SBS polymer, Kraton D1102, except for binder modified with 5% Kraton D1102.

6.1.1.2.2 Asphalt Modified by SIS Polymer

The high service temperature of the binder modified with 3% SIS, Kraton D1107, is the second highest. When the polymer concentration is higher than 3%, the increase of the high service temperature becomes slower. Therefore, at low concentration, the binder modified with Kraton D1107 has a more prominent effect on the improvement of the resistance to permanent deformation than the binder modified with the linear SBS, Kraton D1102 after the RTFO-age.

From the figure 6.1 and 6.2, all the high service temperatures of the binders modified with SIS, Kraton D1107, after aging, are lower than those of binders before aging. Therefore, after aging, the ability of the binders modified with SIS of resistance to permanent deformation decreases.

6.1.1.2.3 Asphalt Modified by EVA Polymers

The high service temperatures of the binders modified with EVA polymers, Elvax 150W and Elvax 350, are the lowest ones compared with the binders modified with the other polymers. From the Figure 6.2, the high service temperature of the binder modified with low concentration of EVA, Elvax 350, with a higher molecular weight and a lower content of vinyl acetate (VA) is higher than the high service temperature of the binder modified with EVA, Elvax 150W, with a lower molecular weight and a higher content of vinyl acetate (VA). When the concentration of polymer is between 3 to 5%, the rate of the increase of the high service temperature of the binder modified with Elvax 350 becomes lower. The high service temperatures of the binders modified with Elvax 350 are lower than the high service temperatures of the binder modified with Elvax 150W when the EVA polymer concentration is between 4% and 5.5%. When the polymer concentration is higher than 5%, the rate of the increase of the high service temperature of the binder modified with Elvax 350 is higher. The binders modified with EVA polymers, Elvax 150W and Elvax 350 have low effect on the improvement of the resistance to permanent deformation of pavement compared to the binders modified with SBS and SIS polymers.

From figure 6.1 and 6.2, the high service temperatures of binders modified with 3 and 5% EVA, Elvax 150W, after aging, are higher than those of binders before aging. Same trend can be seen from the binder modified with 3% EVA, Elvax 350. The binders modified with low concentration of EVA polymers have more improvement of the resistance to permanent deformation after the RTFO-age. This might be caused by larger mass loss (shown in Table 6.2) of the binders modified with EVA polymers, especially at low concentrations, during the RTFO-age. The binders modified with low concentrations of EVA polymers turn harder than those modified with SBS and SIS polymers. Therefore, at high pavement temperatures, the binders modified with EVA polymers become stiffer than those with SBS and SIS polymers, and help to limit the plastic deformation.

6.1.2 RTFO Test

RTFO test is used to simulate the aging during hot mixing /construction. Beside property changes caused by oxidative hardening, the mass loss is another parameter, controlling evaporation of light oils. The results of the mass loss after RTFOT measured for the base asphalt and the polymer modified asphalts are listed in Table 6.2. The details of RTFOT have been described in section 4.4.4.

The results presented in Table 6.2 indicate that all of the binders modified with polymers meet the requirement (mass loss $\leq 1.0\%$). Table 6.2 appears that the mass loss of asphalts modified with EVA is higher than the base asphalt as well as asphalts modified with SBS and SIS. It might be caused by higher absorption of light oils by SBS and SIS polymers.

Table 6.2 Results of RTFO Test

Composition	Mass Loss [%]
200/300 pen base asphalt	0.56
3% radial SBS (Finaprene 411)	0.56
5% radial SBS (Finaprene 411)	0.54
7% radial SBS (Finaprene 411)	0.5
3% linear SBS (Kraton D1102)	0.56
5% linear SBS (Kraton D1102)	0.53
7% linear SBS (Kraton D1102)	0.5
3% SIS (Kraton D1107)	0.54
5% SIS (Kraton D1107)	0.53
7% SIS (Kraton D1107)	0.53
3% EVA (Elvax 150W)	0.73
5% EVA (Elvax 150W)	0.63
7% EVA (Elvax 150W)	0.62
3% EVA (Elvax 350)	0.69
5% EVA (Elvax 350)	0.68
7% EVA (Elvax 350)	0.65

6.2 Effects of Polymer on the Intermediate-Temperature Properties of Asphalts

6.2.1 Dynamic Shear Rheometer Test

According to the SHRP binder specification, the parameter $|G^*|(\sin\delta)$, the loss modulus, is an indicator of the fatigue resistance of asphalt binders. The fatigue cracking is controlled by the value of $|G^*|(\sin\delta)$ on RTFO/PAV aged binders (≤ 5000 kPa) at a specified intermediate temperature. The details of the test have been described in section 4.5.1. The parameter of $|G^*|(\sin\delta)$, loss modulus, and the temperature of the PAV residues at which it was measured are listed in Table 6.3.

Table 6.3 Parameter $|G^*| \sin \delta$ and Temperature for RTFO/PAV Residues

Composition	RTFO/PAV Binder	
	$G^* \sin (\delta)$	Temperature
	(Max. 5000 kPa), [kPa]	[°C]
pen 200/300 base asphalt	4.89	8.1
3% radial SBS (Finaprene 411)	4.97	7
5% radial SBS (Finaprene 411)	4.59	10.1
7% radial SBS (Finaprene 411)	4.85	4.1
3% linear SBS (Kraton D1102)	4.66	7.1
5% linear SBS (Kraton D1102)	4.59	7.9
7% linear SBS (Kraton D1102)	3.1	4
3% SIS (Kraton D1107)	4.86	7.9
5% SIS (Kraton D1107)	4.59	6.9
7% SIS (Kraton D1107)	3.01	4
3% EVA (Elvax 150W)	4.03	4.1
5% EVA (Elvax 150W)	3.2	4
7% EVA (Elvax 150W)	2	4
3% EVA (Elvax 350)	4.99	6.8
5% EVA (Elvax 350)	1.51	4.1
7% EVA (Elvax 350)	3.8	4

The relationships between the temperatures at which $|G^*| \sin \delta$ is just below 5000 kPa and the polymer concentration for PAV-aged 200/300 unmodified and polymer-modified binders are presented in Figure 6.3. Because the lowest temperature at which the instrument can measure is 4.0 °C, it is impossible to measure the temperatures of samples below this value. In this case, the lowest measurable temperatures are listed in Table 6.3. Due to the limitations mentioned above, the results obtained in Table 6.3 and Figure 6.3 are difficult to rationalize. There, however, in most cases it appears a downward trend in this parameter with increasing amount of polymers. Thus, resistance

to fatigue generally increases with increasing amount of polymers.

6.3 Effects of Polymers on the Low-Temperature Properties of Asphalts

6.3.1 Bending Beam Rheometer Test

According to current SHRP binder specification, the stiffness of the material is an indicator of the low temperature cracking of the asphalt binders. The temperatures at which polymer/asphalt blends reach the value of the creep stiffness of 300 MPa are termed “lowest service temperatures” and are presented in Table 6.4. The low temperature cracking is controlled by the creep stiffness (S) on RTFO/PAV aged binders. The m-value (the slope of the log [stiffness] versus log [time] curve) on RTFO/PAV aged binders has to be > 0.300 at 10°C above the minimum pavement design temperature. According to the time-temperature relationship, by raising the testing temperature 10°C , an equal creep stiffness can be obtained after only a 60 second loading. The limiting stiffness temperature (below which low-temperature cracking would occur) is 10°C below the temperature at which the binder reaches this stiffness. If the creep stiffness (S) of RTFO/PAV aged binder exceeds 300 MPa but is less than 600 MPa, direct tension test should be used. The details of the BBR test have been discussed in section 4.4.6, and the results of the BBR tests at a loading time of 60 seconds on RTFOT-aged and PAV-aged binders are summarized in Table 6.4.

The relationship between the low service temperature and the polymer concentration for PAV-aged polymer-modified binders is shown in Figure 6.4. The low service temperatures of the most binders modified with polymers are higher than the low service temperature of the base asphalt, except the binder modified with high concentration of EVA, Elvax 350, with a high molecular weight and a low VA. When the low service temperature is increasing, the resistance to thermal cracking decreases.

Table 6.4 Results of BBR Test

Composition	Creep Stiffness	m-value	T _{low}
	[MPa]		[°C]
pen 200/300 base asphalt	271.4	0.359	-25.9
3% radial SBS (Finaprene 411)	291	0.301	-25.6
5% radial SBS (Finaprene 411)	294.9	0.324	-23
7% radial SBS (Finaprene 411)	289.8	0.303	-23.3
3% linear SBS (Kraton D1102)	283.6	0.323	-25
5% linear SBS (Kraton D1102)	292.1	0.306	-25
7% linear SBS (Kraton D1102)	274.9	0.31	-23.3
3% SIS (Kraton D1107)	295.1	0.309	-25.1
5% SIS (Kraton D1107)	290.6	0.303	-23.1
7% SIS (Kraton D1107)	299.5	0.325	-22
3% EVA (Elvax 150W)	282.8	0.362	-25
5% EVA (Elvax 150W)	271	0.313	-25.5
7% EVA (Elvax 150W)	257.3	0.362	-25.7
3% EVA (Elvax 350)	265.1	0.329	-24.7
5% EVA (Elvax 350)	243.8	0.375	-24.2
7% EVA (Elvax 350)	257.4	0.353	-26.2

The high service temperature and the low service temperature of the binders modified with polymers and the base asphalt are listed in Table 6.5. The difference between the high service temperature ($|G^*|/\sin\delta$ temperature) and low service temperature is an indicator of the temperature susceptibility of binders. A larger difference represents a less temperature susceptibility. The relationship between this temperature difference and the polymer concentration for original (unaged) and RTFOT aged binders are shown in Figure 6.5 and Figure 6.6, respectively. All binders modified with polymers demonstrate a significant increase in the range between high and low service temperatures with the increasing of the polymer concentration, and all of the ranges of the binders modified with polymers are broader than the range of the base

asphalt. The results in Figure 6.5 and Figure 6.6 show that the binders modified with SBS polymers, Finaprene 411 and Kraton D1102, have broader service temperature ranges than the binders modified with SIS and EVA polymers, especially at the high polymer concentrations. The binder modified with SIS has broader temperature range at the low polymer concentrations, and the temperature range tends to be stable after the concentration of SIS is beyond 3%. With regard to the binder modified with EVA, Elvax 150W and Elvax 350, the temperature range of the binder modified with Elvax 350, with a high molecular weight and a low VA is broader than the temperature range of Elvax 150W, with a low molecular weight and a high VA. The above results indicate that all polymer modifiers could be used to improve the temperature susceptibility of binders.

Table 6.5 High and Low Service Temperatures of Studied Polymer/Asphalts

Composition	T _{high}	T _{low}	PG	ΔT
	[°C]	[°C]		[°C]
200/300 pen base asphalt	52	-25.9	52-22	77.9
3% radial SBS (Finaprene 411)	63.1	-25.6	58-22	88.7
5% radial SBS (Finaprene 411)	69.9	-23	70-22	92.9
7% radial SBS (Finaprene 411)	79	-23.3	76-22	102.3
3% linear SBS (Kraton D1102)	60	-25	58-22	85
5% linear SBS (Kraton D1102)	69.2	-25	64-22	94.2
7% linear SBS (Kraton D1102)	74	-23.3	70-22	97.3
3% SIS (Kraton D1107)	61.1	-25.1	58-22	86.2
5% SIS (Kraton D1107)	65	-23.1	64-22	88.1
7% SIS (Kraton D1107)	69.8	-22	70-22	91.8
3% EVA (Elvax 150W)	57	-25	52-22	82
5% EVA (Elvax 150W)	57.9	-25.5	58-22	83.4
7% EVA (Elvax 150W)	63	-25.7	58-22	88.7
3% EVA (Elvax 350)	58	-24.7	58-22	82.7
5% EVA (Elvax 350)	60.9	-24.2	58-22	85.1
7% EVA (Elvax 350)	65.9	-26.2	64-22	92.1

Table 6.5 shows that most of the polymers have significant effects on the high service temperature behavior of polymer/asphalt blends and the effects are more prominent for higher concentration of the polymers. The low temperature properties measured by creep stiffness show tendency to worsen in most cases. However, the creep does not completely describe the low temperature behavior of PMA, and has to be combined with the rheological testing which will be discussed in next chapter.

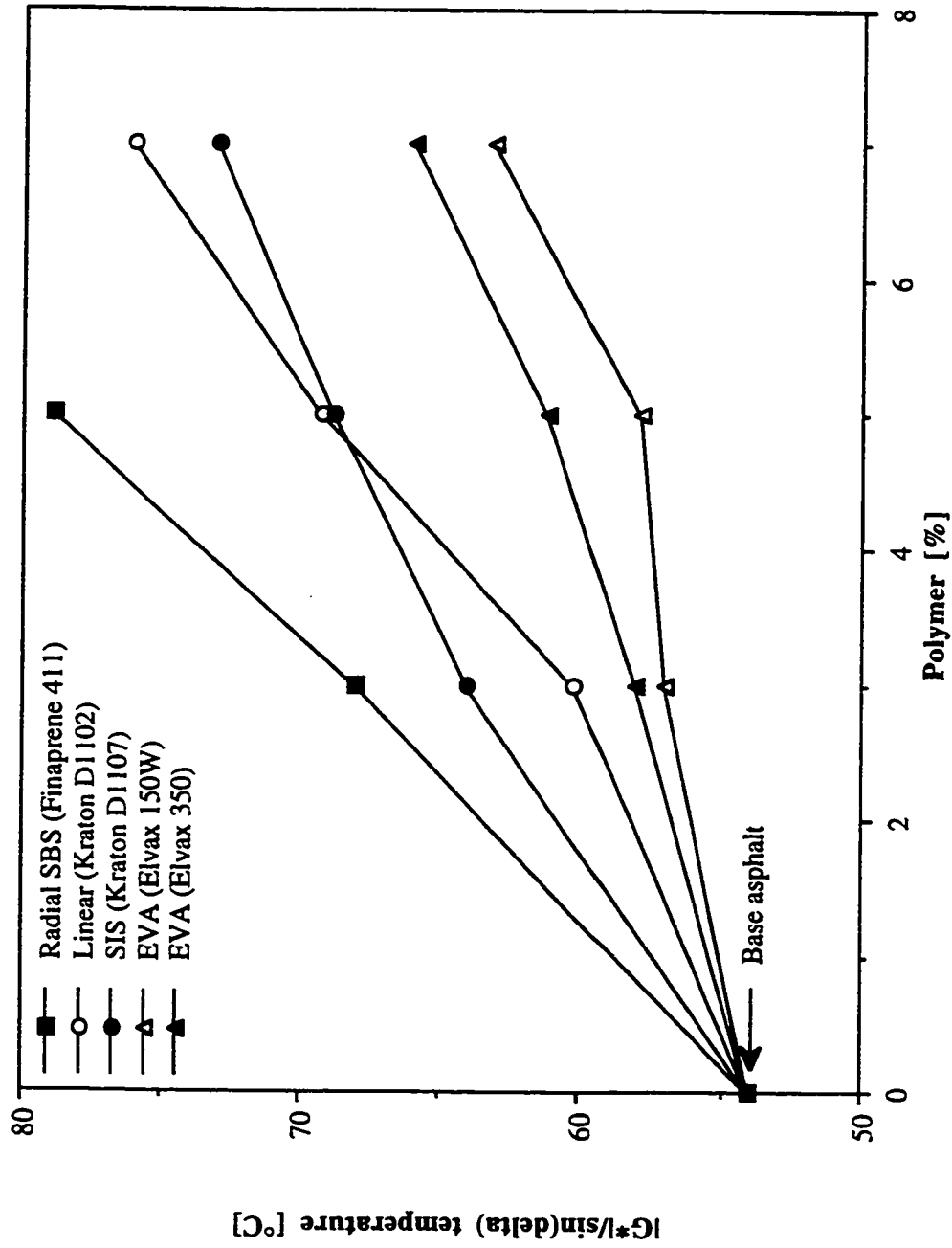


Figure 6.1 G'/G'' vs. Polymer Concentration (Before Aging)

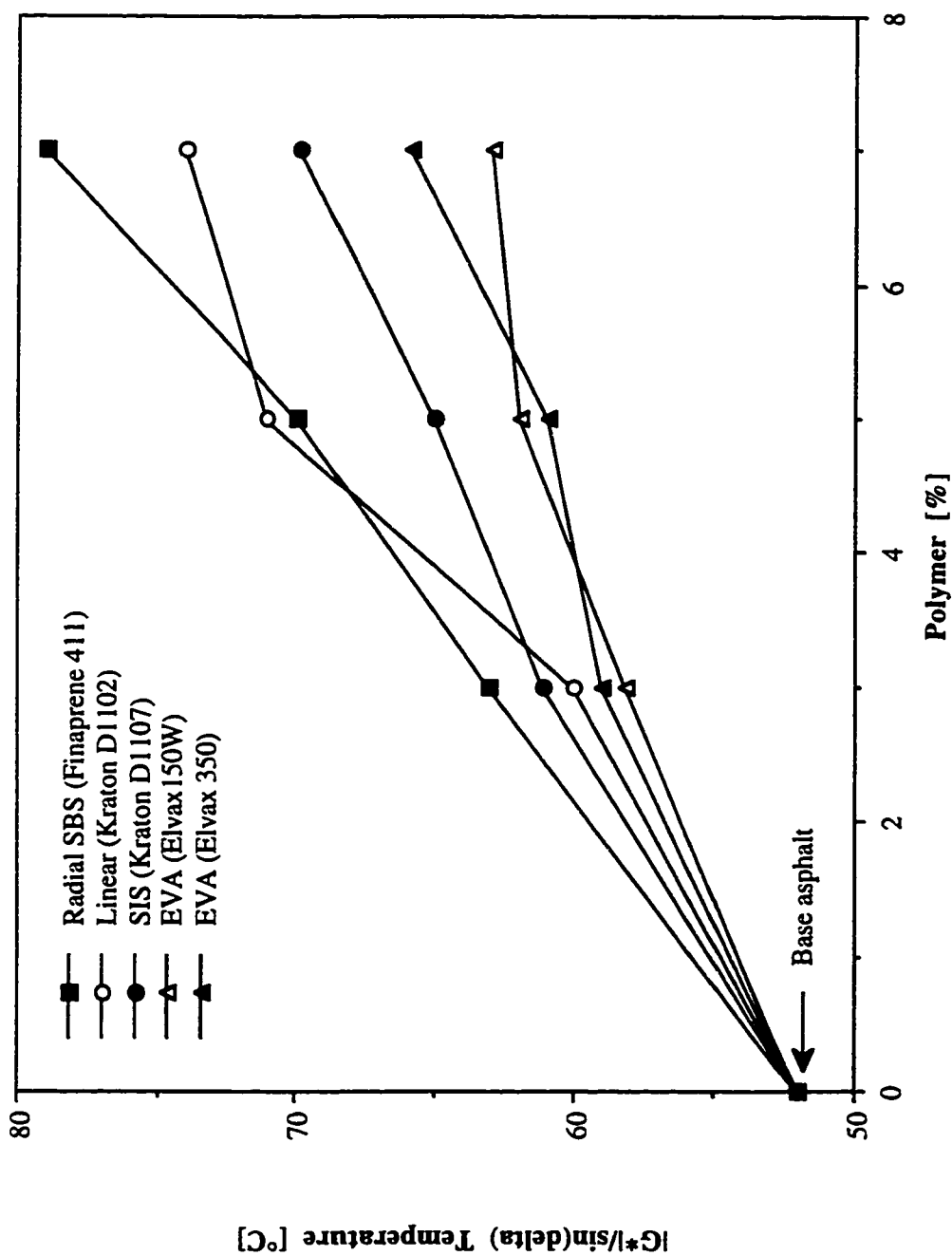


Figure 6.2 |G*/sin(delta) Temperature vs. Polymer Concentration (After Aging)

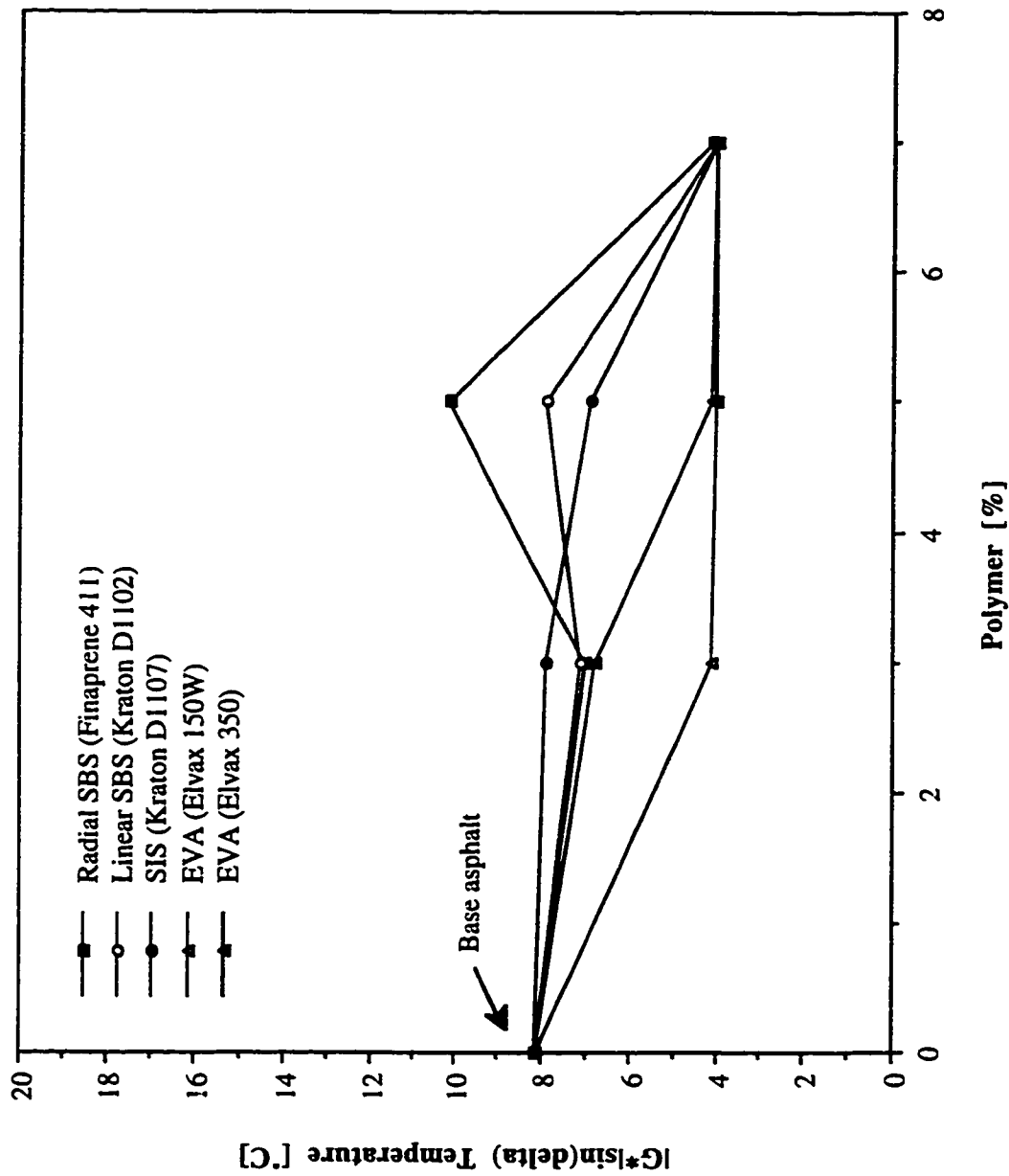


Figure 6.3 $|G^*|\sin(\delta)$ Temperature vs. Polymer Concentration

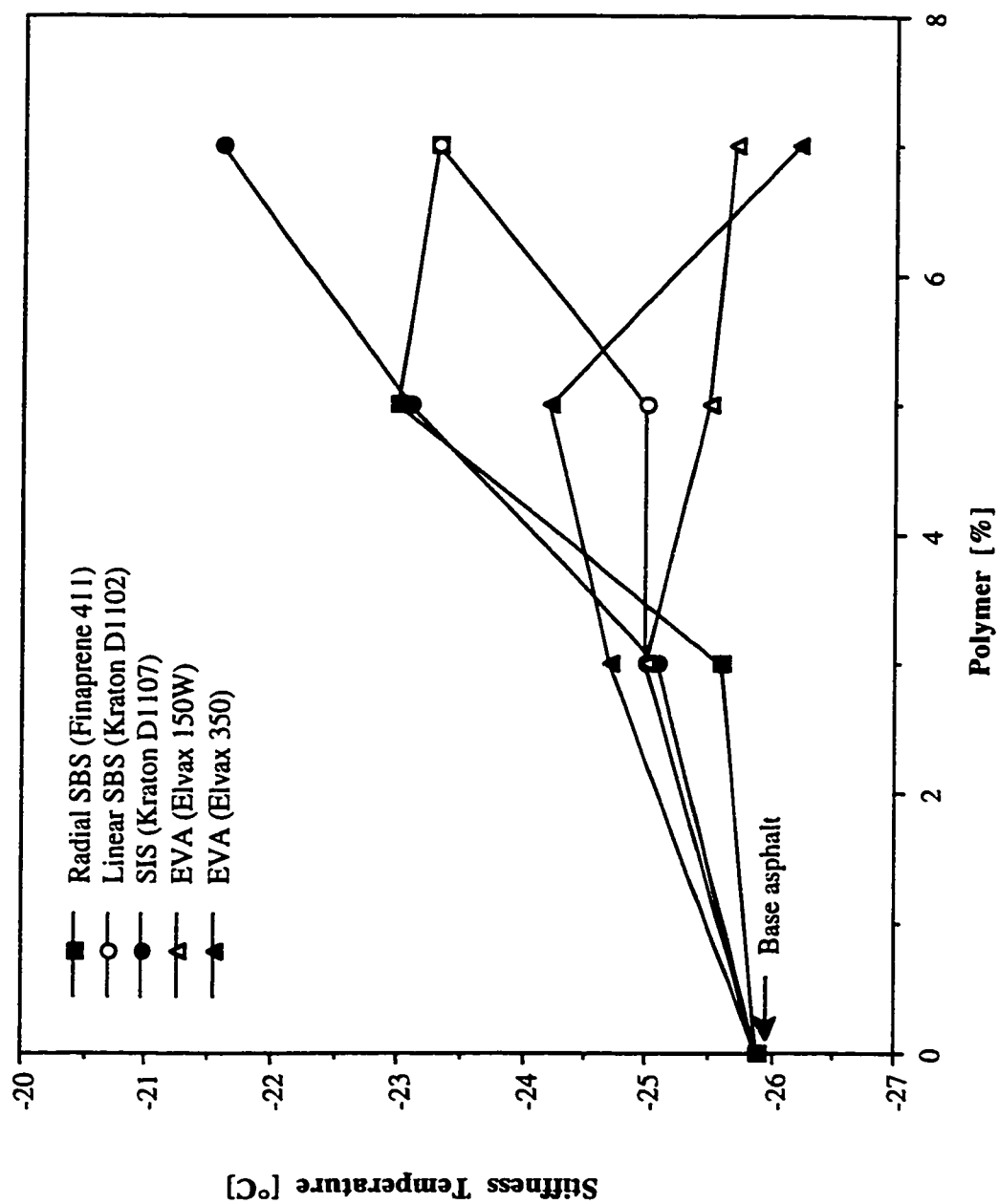


Figure 6.4 Stiffness Temperature vs. Polymer Concentration

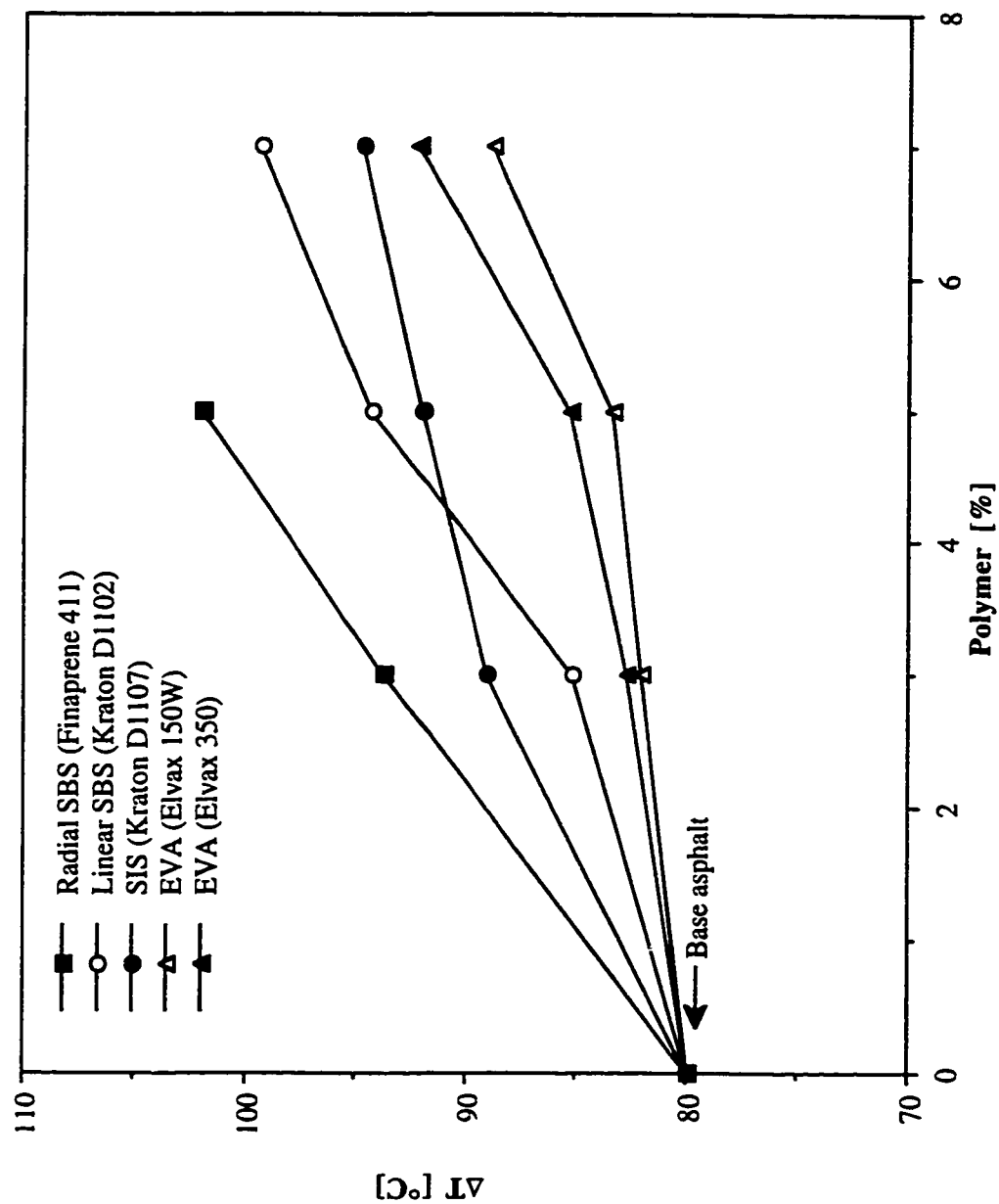


Figure 6.5 Difference of $|G^*|/\sin(\delta)$ Temperature and Stiffness Temperature vs. Polymer Concentration (Before Aging)

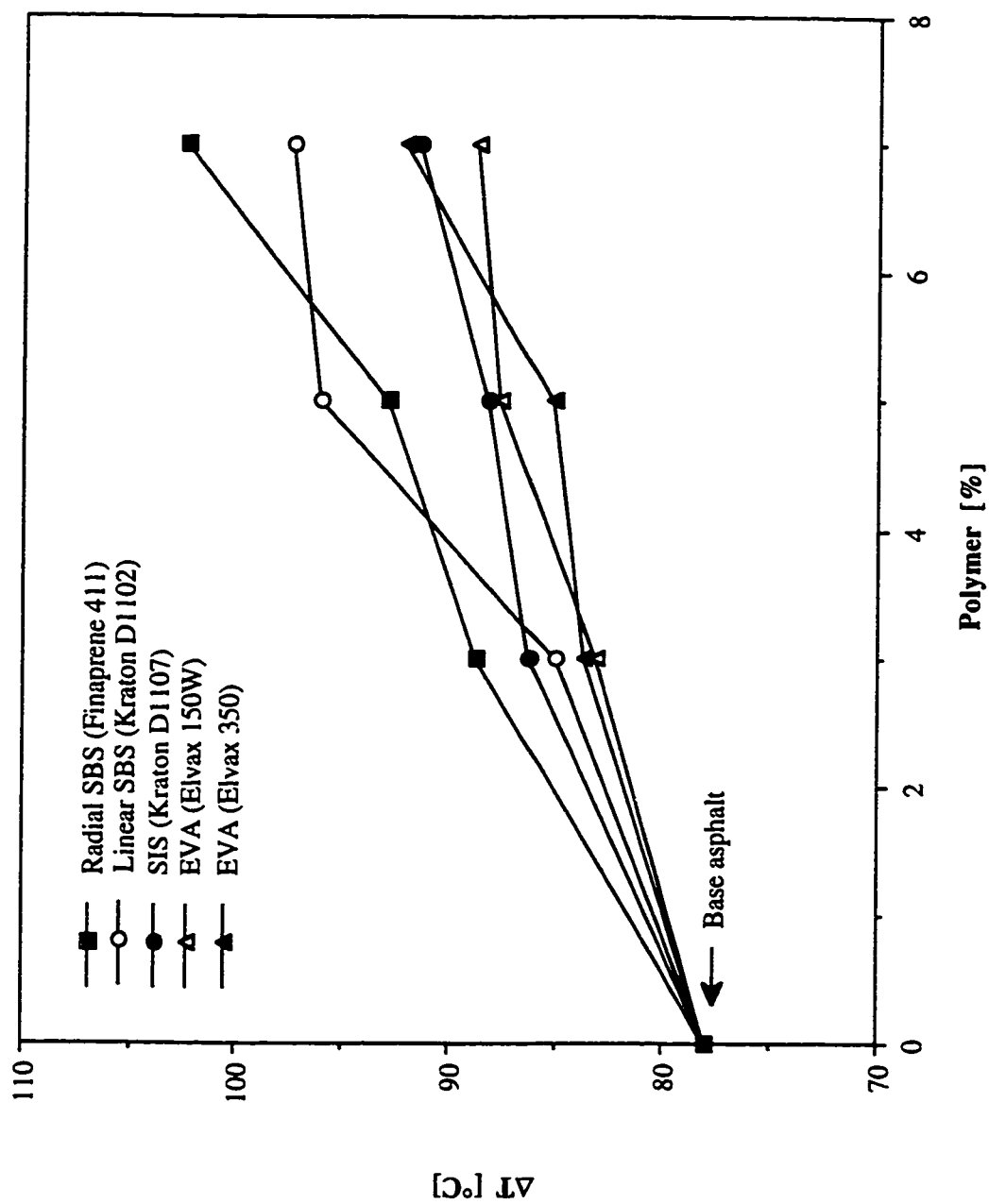


Figure 6.6 Difference of $|G^*|/\sin(\delta)$ Temperature and Stiffness Temperature vs. Polymer Concentration (After Aging)

CHAPTER 7

Rheological Testing of Base and Modified Asphalts

7.1 Dynamic Material Functions

Various components of the complex modulus $G^*(\omega)$ of the studied materials (dynamic material functions) have been measured in the linear viscoelastic region. The measurements were performed at different temperatures and the master curves of various dynamic material functions have been prepared.

7.1.1 Master Curve

In order to construct a master curve, it is necessary to shift the sets of dynamic mechanical data along the log-frequency axis either by automatic shifting or by manual shifting. The shifting was done with the help of the commercial software-IRIS. In general, this procedure did result in fairly smooth and continuous functions for both components of G^* , the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$. For example, Figure 7.1 shows the unshifted components of the complex modulus for the binder modified with 5% radial SBS, Finaprene 411. The resulting master curves of G' , and G'' at the reference temperature 5 °C, are shown in Figure 7.2. The independent variable is the reduced frequency, $a_T\omega$. Here a_T is the shift factor which was obtained by manual shifting inside the IRIS software.

7.1.2 Shift Factor

For the studied materials, the shift factors can be described by both the Williams-Landel-Ferry equation or the Arrhenius equation that are discussed in section 2.2.1.3. Both equations seem to be suitable for the modified and the base asphalt binders. However, the WLF equation gives better fit for the binders studied in this thesis.

Therefor only the WLF equation is selected as the temperature dependence model. For example, Figure 7.3 shows the fit of a_T for the binder modified with 5% Finaprene 411. The parameters C1 and C2 for the WLF equation are 16.42 and 115.1, respectively. All the master curves presented in this work are shifted to the reference temperature 5 °C. Most of them use only the horizontal shifting, except one binder modified with 5% Elvax 350 where the vertical shifting was necessary.

7.1.3 Master Curves of The Studied Materials

The shapes of dynamic master curves generally depend on the structural properties of the studied materials. Thus the base asphalt, the type of polymer, its concentration and their physical properties might be reflected in the obtained master curves. All master curves referred in this work, are shifted to the reference temperature $T_{ref} = 5$ °C.

7.1.3.1 Base Asphalt

The base asphalt is 200/300 pen grade. The shift factors of the base asphalt are shown in Table 7.1. The shift factor associated with master curve of the binder is displayed in Figure 7.4. No vertical shifting is necessary. From Figure 7.4, it is observed that the data can be fitted by WLF equation very well. The value of r^2 is 0.9993. The values of parameters C1 and C2, for the logarithm of the shift factor ($\log a_T$) are 13.88 and 86.5, respectively.

Figure 7.5 shows the master curves of G' and G'' of the base asphalt 200/300 pen grade. The range of the reduced frequency is between 1×10^{-5} rad/s and 11 rad/s. The maxima of G' and G'' are 1×10^6 Pa and 2×10^6 Pa, respectively. The minima of G' and G'' are 8×10^{-2} Pa and 15 Pa, respectively. Different regimes, which depend on the different slopes of master curves, can be observed. However, it is obvious that no inflections or plateaus are formed.

Table 7.1 Shift Factors for Base Asphalt

No.	Temperature [°C]	log a_T
1	5	0
2	10	-0.67
3	20	-2.08
4	30	-3.15
5	40	-3.97
6	45	-4.39

7.1.3.2 Asphalt modified by SBS Polymers

One of the SBS studied in this work is the high molecular weight radial SBS polymer, Finaprene 411. The shift factors of binder modified with 3% of Finaprene 411 are shown in Table 7.2. The shift factor associated with the master curve of this sample is shown in Figure 7.6. No vertical shifting is needed. It is observed that the curve can be fitted well with the WLF equation. The value of r^2 is 0.9940. The values of parameters C1, and C2 for the logarithm of the shift factor (log a_T) are 12.63 and 80.24, respectively.

Table 7.2 Shift Factors for Binder Modified with 3% Radial SBS, Finaprene 411

No.	Temperature [°C]	Log a_T
1	5	0
2	10	-0.66
3	20	-2.28
4	30	-2.84
5	40	-3.74
6	50	-4.51
7	60	-5.22

Figure 7.7 portrays the storage modulus G' , and the loss modulus G'' versus reduced frequency $a_T \omega$ of this modified binder at low concentration of polymer, 3%. From the figures, we observe that both G' and G'' increase with the increase of reduced frequencies. G'' is larger than G' . Figure 7.7 also shows that for the binder modified with 3% radial SBS, Finaprene 411, the obtained range of the reduced frequency is between 9×10^{-7} rad/s and 10 rad/s. The maxima of G' and G'' are 2×10^6 Pa and 3×10^6 Pa, respectively. The minima of G' and G'' are 0.7 Pa and 10.3 Pa, respectively. It appears that there are three different slopes in G' , and G'' seems to have only two different slopes. A “weak” inflection occurs on G' curve, at low frequencies.

The shift factors of the binder modified with 5% radial SBS are shown in Table 7.3. The shift factor associated with master curve of the binder is displayed in Figure 7.3. No vertical shifting is necessary. It is observed the data can be fitted well by the WLF equation. The value of r^2 is 0.9936. The parameters C_1 , and C_2 are 16.43 and 115.1, respectively.

Table 7.3 Shift Factors for Binder Modified with 5% Radial SBS Finaprene 411

No.	Temperature [°C]	$\log a_T$
1	5	0
2	10	-0.58
3	20	-1.62
4	30	-3.18
5	40	-3.9
6	50	-4.62
7	60	-5.24

Figure 7.2 portrays the storage modulus G' , and the loss modulus G'' versus the reduced frequency $a_T \omega$ of the binder modified with 3% SBS. From this figure, it is observed that both G' and G'' increase with the increase of reduced frequencies. G'' is larger than G' . The range of the reduced frequencies is between 2×10^{-7} rad/s and 20 rad/s.

The maxima of G' and G'' are 4.5×10^6 Pa, 5×10^6 Pa, respectively. The minima of G' and G'' are 4×10^{-2} Pa and 9×10^{-1} Pa, respectively. There are at least three different regimes as indicated by the different slopes in G' . The inflection of G' is observed at low reduced frequencies.

The other SBS polymer used in this work is a linear SBS polymer, Kraton D1102. The shift factors of the binder modified with 3% of linear SBS are shown in Table 7.4. The shift factor associated with the master curve of this sample is shown in Figure 7.8. The data can be fitted well with the WLF equation. The value of r^2 is 0.9973. The parameter C_1 , and C_2 are 13.48 and 71.88, respectively.

Table 7.4 Shifts Factor for Binder Modified with 3% Linear SBS Kraton D1102

No.	Temperature [°C]	$\log a_T$
1	5	0
2	10	-0.83
3	20	-2.52
4	35	-3.91
5	40	-4.33
6	50	-5.08
7	60	-5.98

Figure 7.9 shows G' and G'' of the binder modified with 3% linear SBS, Kraton D1102. Both G' and G'' increase with the increasing reduced frequencies. G'' is larger than G' . In this figure, the range of the reduced frequency is between 3×10^{-7} rad/s and 20 rad/s. The maxima of G' and G'' are 1×10^6 Pa and 2×10^6 Pa, respectively. The minima of G' and G'' are 3×10^{-2} Pa and 0.9 Pa, respectively. There are three regimes observed, from the curve G' . In the low frequencies, a “weak” inflection is observed in storage modulus G' .

The shift factors of the binder modified with 5% linear SBS, Kraton D1102, are

shown in Table 7.5. The shift factor associated with master curve of the binder is displayed in Figure 7.10. The data are fitted well with WLF equation. The value of r^2 is 0.9917. The parameters C_1 , and C_2 are 1.0×10^8 and 1.0×10^9 , respectively.

Table 7.5 Shift Factors for Binder Modified with 5% Linear SBS Kraton D1102

No.	Temperature [°C]	$\log a_T$
1	5	0
2	10	-0.6
3	15	-1.28
4	30	-2.41
5	40	-3.42
6	50	-4.31
7	60	-5.13
8	70	-6.75

Figure 7.11 displays the G' and G'' versus reduced frequency for the binder modified with 5% of linear SBS. The loss modulus G'' is greater than the storage modulus G' . The range of the reduced frequency is between 3×10^{-8} rad/s and 20 rad/s. The maxima of G' and G'' are 1.8×10^6 Pa and 2×10^6 Pa, respectively. The minima of G' and G'' are 2×10^{-2} Pa and 0.9 Pa, respectively. There are three different regimes observed in G' (characterized by different slopes).

7.1.3.3 Asphalt Modified by SIS Polymer

The shift factors of the binder modified with 3% SIS, Kraton D1107, are shown in Table 7.6. The shift factor associated with master curve of the binder is displayed in Figure 7.12. The data are fitted excellently with WLF equation. The value of r^2 is 0.9994, and the values of parameters C_1 , and C_2 are 17.81 and 136.6, respectively.

Table 7.6 Shift Factors for Binder Modified with 3% SIS Kraton D1107

No.	Temperature [°C]	$\log a_T$
1	5	0
2	10	-0.58
3	20	-1.69
4	30	-2.8
5	40	-3.68
6	50	-4.42
7	60	-5.08

Figure 7.13 shows G' and G'' of the binder modified with 3% of SIS, Kraton D1107. As seen from Figure 7.13, G'' is greater than G' , and G' and G'' are increasing functions of reduced frequencies. The range of the reduced frequency is between 3×10^{-6} rad/s and 20 rad/s. The maxima of G' and G'' are 4×10^6 Pa and 5×10^6 Pa, respectively. The minima of G' and G'' are 6 Pa and 80 Pa, respectively. At least three regimes are observed in G' . The inflection is observed at low frequencies on the curve G' .

The shift factors of the binder modified with 5% SIS, Kraton D1102, are shown in Table 7.7. The shift factor associated with master curve of the binder is displayed in Figure 7.14. The data are fitted well with WLF equation. The value of r^2 is 0.9918, and the parameters C_1 , and C_2 are 1.1×10^{14} and 8.5×10^{14} , respectively.

Figure 7.15 shows G' , and G'' of the binder modified with 5% of SIS, Kraton D1107. Again, G'' is greater than G' , and both are increasing functions of reduced frequencies. The range of the reduced frequency is between 7×10^{-9} rad/s and 20 rad/s. The maxima of G' and G'' are 2×10^6 Pa and 2.01×10^6 Pa, respectively, and they almost coincide. The minima of G' and G'' are 3×10^{-2} Pa and 7×10^{-1} Pa, respectively. Three different regimes can be recognized from the graphs of G' and G'' .

Table 7.7 Shift Factors for Binder Modified with 5% SIS Kraton D1107

No.	Temperature [°C]	log a_T
1	5	0
2	10	-0.56
3	20	-1.74
4	30	-2.7
5	40	-4.35
6	50	-5.93
7	60	-7.22

7.1.3.4 Asphalt Modified by EVA Polymers

In constructing the master curves of the binder modified with 3% EVA, Elvax 350, both vertical and horizontal shift factors are necessary. The shift factors of the binder modified with 3% Elvax 350, are shown in Table 7.8. The horizontal and vertical shift factors associated with master curves of the binder are displayed in Figure 7.16 and Figure 7.17. The data can be fitted well with the WLF model. The value of r^2 is 0.9961 (horizontal), and 0.9997 (vertical), respectively. The parameters C_1 , and C_2 for horizontal shifting are 13.1 and 59.65, respectively. The parameters C_1 , and C_2 for vertical shifting are 1.625 and 26.87, respectively.

Figure 7.18 shows G' and G'' of the binder modified with 3% of EVA, Elvax 350. The loss modulus G'' is greater than G' , and both increase with the increasing reduced frequencies. The range of the reduced frequency is between 3×10^{-7} rad/s and 20 rad/s. The maxima of G' , and G'' are 3×10^6 Pa and 4×10^6 Pa, respectively. The minima of G' and G'' are 6×10^{-1} Pa and 6 Pa, respectively. There are three regimes observed in G' . The inflection of G' is observed when the frequencies are low.

Table 7.8 Shifts Factors for Binder Modified with 3% EVA Elvax 350

No.	Temperature [°C]	$\log a_T$	$\log b_T$
1	5	0	0
2	10	-0.85	-0.21
3	20	-2.85	-0.6
4	30	-4.05	-0.82
5	40	-4.93	-0.9
6	50	-5.38	-0.10
7	60	-6.38	-1.1

The shift factors of the binder modified with 5% EVA, Elvax 350, are shown in Table 7.9, and the graph of a_T is displayed in Figure 7.19. The data can be fitted to the WLF model. The value of r^2 is 0.9748, and the parameters C_1 , and C_2 are 47.5 and 373.9, respectively.

Table 7.9 Shift Factors for Binder Modified with 5% EVA Elvax 350

No.	Temperature [°C]	$\log a_T$
1	5	0
2	10	-0.7
3	20	-1.3
4	30	-3.22
5	40	-4.41
6	50	-4.87

Figure 7.20 shows G' and G'' of the binder modified with 5% of EVA, Elvax 350. G'' is greater than G' , and both are increasing with the increase of reduced frequencies. The range of the reduced frequency is between 2×10^{-6} rad/s and 20 rad/s. The maxima of G' and G'' are 4×10^5 Pa and 7×10^5 Pa, respectively. The minima of G' and G'' are 2 Pa and 10 Pa, respectively. The three different regimes can be observed in

G' , these are characterized by different slopes of the graph of G' . An inflection appears at low frequencies on the graph of G' .

7.1.4 Comparison of Storage Moduli (G')

The storage modulus (G') is a measure of the energy stored and recovered per cycle, when different systems are compared at the same strain amplitude (Ferry, 1981). Higher G' at low frequencies (high temperatures) leads to the higher resistance to permanent deformations (Bonemazzi, 1996).

7.1.4.1 Asphalt Modified by SBS Polymers

Figure 7.21 shows G' of the binders modified with different concentrations (3% and 5%) of radial SBS polymer, Finaprene 411, at the reference temperature 5 °C. The reduced frequency domain is, 1×10^{-5} rad/s to 20 rad/s. It is seen that there is an increase in G' with the increase of the concentration of radial SBS polymer, Finaprene 411. This increase is strongest at low reduced frequencies.

Similar trend holds for the storage moduli G' , Figure 7.22, of the binders modified with three different concentration of linear SBS polymer, Kraton D1102, except at the reduced frequencies higher than 0.1 rad/s. When the range of reduced frequencies is from 0.1 rad/s to 20 rad/s, the storage modulus of the binder modified with 3% SBS converges to the one of the base asphalt. In the reduced frequency range from 1×10^{-5} rad/s to 0.1 rad/s, the order of magnitudes of G' is: 5% linear SBS > 3% linear SBS > base asphalt.

7.1.4.2 Asphalt Modified by SIS Polymer

The storage moduli, G' , of the binders modified with different concentrations of SIS, Kraton D1107, are shown in Figure 7.23. In the reduced frequency range from 1×10^{-5} rad/s to 20 rad/s, the storage moduli of the binders modified with 3% and 5% SIS are higher than those of the base asphalt. When the reduced frequency is lower than 0.1 rad/s, the order of magnitudes of G' is: 5% SIS > 3% SIS > base asphalt. When the

reduced frequency is higher than 0.1 rad/s, the sequence is changed to: 3% SIS > 5% SIS > base asphalt.

7.1.4.3 Asphalt Modified by EVA Polymers

The storage moduli, G' , of the binders modified with different concentrations of EVA, Elvax 350, are shown in Figure 7.24. When the reduced frequency range is from 1×10^{-5} rad/s to 0.5 rad/s, the G' for the binder modified with 3% and 5% EVA is higher than that of base asphalt. When the reduced frequency is higher than 0.5 rad/s, the order of magnitudes of G' , for these binders is: 3% EVA > base asphalt > 5% EVA. When the reduced frequency is lower than 0.5 rad/s, the sequence of magnitudes of G' is: 3% EVA > 5% EVA > base asphalt.

Overall, the results for the storage moduli (G') of binders modified with SBS, SIS, and EVA polymers are in agreement with the storage modulus G' of an amorphous polymer with a low molecular weight (Ferry, 1980).

7.1.5 Comparison of Loss Moduli (G'')

The loss modulus (G'') is a measure of the energy lost or heat per cycle of sinusoidal deformation, when different systems are compared at the same strain amplitude (Ferry, 1981). Higher G'' at high frequencies (low temperatures) leads to better low-temperature flexibility (Bonemazzi, 1996).

7.1.5.1 Asphalt Modified by SBS Polymers

Figure 7.25 portrays G'' for the binders modified with different concentrations of the radial SBS, Finaprene 411. It is observed that G'' increases with the increase of the polymer concentration, especially at low frequencies. In the reduced frequency range from 1×10^{-5} rad/s to 20 rad/s, the loss moduli, G'' , of the binders modified with 3%, and 5% radial SBS are higher than the one of the base asphalt. In the same range, the order of magnitudes of G'' is: 5% radial SBS > 3% radial SBS > base asphalt.

The loss moduli, G'' , of the binders modified with different concentrations of linear SBS, Kraton D1102, are displayed in Figure 7.26. When the reduced frequency range is from 1×10^{-5} rad/s to 0.02 rad/s, the loss moduli G'' of the binders modified with 3%, and 5% linear SBS are higher than the one of the base asphalt. When the reduced frequency is lower than 0.02 rad/s, the order of magnitudes of G'' is: 5% linear SBS > 3% linear SBS > base asphalt. When the reduced frequency is higher than 0.02 rad/s, the sequence is changed to: 5% linear SBS > base asphalt > 3% linear SBS.

7.1.5.2 Asphalt Modified by SIS Polymer

The loss moduli, G'' , of the binders modified with different concentrations of SIS Kraton D1107, are displayed in Figure 7.27. When the reduced frequency range is from 1×10^{-5} rad/s to 10 rad/s, the loss modulus of the base asphalt is lower than that of the binders modified with 3%, and 5% SIS. When the reduced frequency is lower than 6×10^{-3} rad/s, the order of magnitudes of G'' for the binders modified with SIS is: 5% SIS > 3% SIS > base asphalt. When the reduced frequency is higher than 6×10^{-3} rad/s and lower than 10 rad/s, the sequence is changed to: 3% SIS > 5% SIS > base asphalt. When the reduced frequency is higher than 10 rad/s, the order of magnitudes of G'' is: 3% SIS > base asphalt > 5% SIS.

7.1.5.3 Asphalt Modified by EVA Polymers

The loss moduli, G'' , of the binders modified with different concentrations of EVA, Elvax 350, are shown in Figure 7.28. When the reduced frequency range is from 1×10^{-5} rad/s to 0.03 rad/s, the loss modulus G'' of the base asphalt is lower than that of the binders modified with 3%, and 5% EVA. When the reduced frequency is lower than 0.03 rad/s, the order of magnitudes of G'' is: 3% EVA > 5% EVA > base asphalt. For reduced frequencies higher than 0.03 rad/s, the sequence of magnitudes of G'' is: 3% EVA > base asphalt > 5% EVA.

Overall, the results for the loss modulus (G'') of the binders modified with SBS, SIS, and EVA polymers agree with the results obtained for an amorphous polymer with a

low molecular weight (Ferry, 1980). At very low frequencies, G'' for a viscoelastic liquid should be directly proportional to ω .

7.1.6 Comparison of the Loss Tangents

The loss tangent ($\tan \delta = G''/G'$) is a dimensionless parameter which is a measure of the ratio of energy lost to energy stored in a harmonic deformation (Ferry, 1981). The loss tangent represents one of the key parameters which can help in predicting the asphalt performance at high temperatures. Small $\tan \delta$ at high temperature (low frequencies) demonstrates good elastic response (Bonemazzi, 1996; Shuler, et al, 1985).

7.1.6.1 Asphalt Modified by SBS Polymers

It can be seen from Figure 7.29 that the behaviour of the base asphalt is very much different from the behaviour of binders modified with polymers. A strong increase of the loss tangent, for the base asphalt, at lower frequencies, demonstrates the Newtonian behaviour (this frequency region corresponds to the temperatures higher than 50 °C). The binders modified with 3%, and 5% concentrations of the radial SBS exhibit very different behaviour. For both binders there are small local maxima of $\tan \delta$, around the reduced frequency 0.1 rad/s. Both binders also exhibit a local minima of $\tan \delta$ around the reduced frequency 0.001 rad/s. For the reduced frequencies lower than 0.001 rad/s, the binder modified with 5% radial SBS has a relatively strong local maximum of $\tan \delta$ around the reduced frequency 10^{-6} rad/s. The similar local maximum, for the binder modified with 3% radial SBS, is much weaker and is probably shifted to the range of 10^{-5} rad/s, of the reduced frequency. Interesting is the decrease of $\tan \delta$, for the binder modified with 5% radial SBS, at very low frequencies ($< 10^{-6}$ rad/s), such a decrease represents the increase in elasticity of this sample at high temperatures. Similar behaviour is observed for the binder modified with 3% of a linear SBS, Figure 7.30. Here the local maximum of $\tan \delta$, at roughly 5×10^{-6} rad/s, is followed by a decrease of $\tan \delta$ (with a local minimum around 10^{-6} rad/s). For even lower reduced frequencies the loss tangent of this sample is steadily increasing. None of this behaviour is observed for the binder modified with 5% of a linear SBS polymer. Here the loss tangent is increasing

with decreasing reduced frequency almost steadily.

7.1.6.2 Asphalt Modified by SIS Polymer

It can be seen from Figure 7.31 that the behaviour of the base asphalt is very much different from the behaviour of binders modified with SIS polymer. A strong increase of the loss tangent, for the base asphalt, at lower frequencies, demonstrates the Newtonian behaviour (this frequency region corresponds to the temperatures higher than 50 °C). The binders modified with 3%, and 5% of the SIS, Kraton D1107, exhibit very different behaviour. For the binder modified with 3% SIS, there is a strong local maximum of $\tan \delta$, around the reduced frequency 1×10^{-5} rad/s, followed by a decrease of $\tan \delta$, at very low frequencies ($< 9 \times 10^{-6}$ rad/s), such a decrease represents the increase in elasticity of this sample at high temperatures. None of this behaviour is observed for the binder modified with 5% SIS polymer. Here the loss tangent is increasing with decreasing reduced frequency almost steadily, at least at the measured domain of temperatures.

7.1.6.3 Asphalt Modified by EVA Polymers

It can be seen from Figure 7.32 that again the behaviour of the base asphalt is very much different from the behaviour of modified asphalt binders. A strong increase of the loss tangent, for the base asphalt, at lower frequencies, demonstrates the Newtonian behaviour (this frequency region corresponds to the temperatures higher than 50 °C). The binders modified with 3%, and 5% of EVA, Elvax 350, exhibit very different behaviour. For the binder modified with 5% Elvax 350, there is a small local maximum of $\tan \delta$, around the reduced frequency 0.9 rad/s. The binder modified with 5% Elvax 350 also exhibits a local minimum of $\tan \delta$ around the reduced frequency 0.08 rad/s. For the reduced frequencies lower than 1×10^{-4} rad/s, the binder modified with 5% Elvax 350 has another small local maximum of $\tan \delta$ around the reduced frequency 1×10^{-5} rad/s. The similar local maximum, for the binder modified with 3% Elvax 350, is much stronger and is probably shifted to the range of 1×10^{-6} rad/s, of the reduced frequency. Very small decrease of $\tan \delta$, for the binder modified with 5% Elvax 350, at very low frequencies

(< 5×10^{-6} rad/s) indicates a small increase in elasticity of this sample at high temperatures. These changes are very small and most probably one can say that the loss tangent of these two binders modified EVA is almost constant at the lower end of the given reduced frequency window.

It is seen from Figures 7.29-7.32, that the base asphalt behaves similarly as an amorphous polymer (uncross-linked) of low molecular weight (Ferry, 1980). The loss tangent of all the studied modified binders is lower than the loss tangent of the base asphalt. This difference is especially large at low reduced frequencies. Several modified binders show a behaviour of a crystalline-like material (probably lamellae or fibrils form a weak matrix of this material). These are: binder modified by 5% of radial SBS, Figures 7.29, and binder modified by 5% EVA, Figure 7.32. These materials are characterized by low values of loss tangent, at low reduced frequencies, and by the presence of a small local maximum of the loss tangent, at this domain. The presence of a small local maximum, of the loss tangent, at higher reduced frequencies points to a lightly cross-linked material. This behaviour can be detected in Figure 7.29, for the modified binders (3%, and 5% radial SBS), and in Figure 7.30 for the binder modified by 3%, and 5% of linear SBS. No such a behaviour is detected for binders modified by SIS and EVA. These observations, made from the graphs of the loss tangent, are only barely visible on the graphs of the storage and loss moduli. This might mean that the loss tangent is the most important material function, which reflects the structural properties of bituminous systems (at least for the studied low concentrations of the given group of polymers).

7.1.7 The Effect of Polymer on Elasticity of Modified Binders

The elasticity of asphalts can be dramatically enhanced when modified with polymer, and thus the system recovers to a much higher degree after a given loading (it is less susceptible to permanent deformation), as discussed above. Bouldin et al. (1991) have suggested two ratios which may help in determining the effectiveness of a polymer modification for asphalt binders, as shown in Table 7.10. These ratios are: 1) $G'T$, a comparison of the storage (elastic) modulus for the modified binders at room temperature

30°C (G'_{30}) versus that at 60°C (G'_{60}), and 2) G'_m/G'_u , a comparison of the storage (elastic) modulus for the modified binders (G'_m) versus that of the unmodified materials (G'_u) at 60°C which is close to the maximum service temperature of many roads. These moduli are measured at a frequency of 1 rad/s, which may approximate truck traffic conditions (Bouldin et al., 1991). The first ratio is a measure of the temperature susceptibility of the elasticity of the system, whereas the second ratio gives us a feeling for how much the elasticity has been boosted by the addition of the polymer. The lower the $G'T$ is, the lower the temperature susceptibility of binder is. The higher the G'_m/G'_u is, the more effect of polymer on the elasticity of the binder is. Therefore, the small values of GT' and large values of G'_m/G'_u are expected for the polymer modified binders.

Table 7.10 Influence of Polymer on Elasticity

Polymer	Content	G' , [Pa]	G' , [Pa]	$G'T$	G'_m/G'_u
	%w	T=30 °C, $\omega=1$ rad/s	T=60 °C, $\omega=1$ rad/s		
none	0	401	0.82	491.42	none
radial SBS (Finaprene 411)	3	4820	24.72	194.98	30.29
linear SBS (Kraton D1102)	3	2535	13.59	186.53	16.65
SIS (Kraton D1107)	3	5937	15.9	373.40	19.49
EVA (Elvax 350)	3	2748	14.15	194.20	17.34
radial SBS (Finaprene 411)	5	8734	254.1	34.37	311.40
linear SBS (Kraton D1102)	5	8940	110	81.27	134.80
SIS (Kraton D1107)	5	9070	55.7	162.84	68.26
EVA (Elvax 350)	5	4093	31.63	129.40	38.76

At low concentration of polymers, e.g. 3% of polymers, the rank by $G'T$ is: linear SBS (Kraton D1102) < radial SBS (Finaprene 411) \cong EVA (Elvax 350) < SIS (Kraton D1107). The binder modified with linear SBS shows significantly reduced temperature

susceptibility relative to the same base asphalt binder modified with 3% of other polymers, especially the binder modified with SIS polymer. All of them, however, exhibit significant improvement compared to the base asphalt. At the high concentration (5%) of polymers, the rank by $G'T$ is: radial SBS (Finaprene 411) < linear SBS (Kraton D1102) < EVA (Elvax 350) < SIS (Kraton D1107). The binder modified with 5% SBS, Finaprene 411, shows a strongly reduced temperature susceptibility relative to the same base asphalt binder modified with 5% of other polymers, especially the binder modified with SIS polymer, Kraton D1107. All of them, however, exhibit dramatic improvement compared to the base asphalt.

In addition, the rank by the value of $G'm/G'u$ for the binders modified with 3% polymers is radial SBS (Finaprene 411) > SIS (Kraton D1107) > EVA (Elvax 350) > linear SBS (Kraton D1102). The binder modified with 3% of radial SBS, Finaprene 411, is found to have increased the elasticity at 60°C ($\omega=1$ rad/s) most, in comparison to other binders. For the binders modified with 5% polymers, the rank by the value of $G'm/G'u$ is radial SBS (Finaprene 411) > linear SBS (Kraton D1102) > SIS (Kraton D1107) > EVA (Elvax 350). The binder modified with 5% radial SBS shows the highest increase of elastic properties from all asphalt binders. Although the binders modified with 3% Finaprene 411, and Elvax 350, show the same significantly reduced temperature susceptibility, compared to the base asphalt, the binder modified with Finaprene 411 improves the elasticity of binders the most with the increase of its concentration whereas EVA polymer (Elvax 350) improves elasticity much less (Table 7.10). Among all of the polymers used in this study, SIS polymer (Kraton D1107) has the least effects on the temperature susceptibility and elasticity of binders.

7.18 Polymer/Asphalt Compatibility and Viscoelastic Properties of Blends

Compatibility is one of the critical properties of polymer-modified asphalts. It can be characterized by the nature of the continuous phase and the fineness of the dispersion of the discontinuous phase, and it is considered to be optimum. The coarse dispersion and solution are considered to be the worst scenario (Beem and Brassar, 1973).

7.1.8.1 Binders Modified with SBS Polymers

At the microscopic level, all binders modified with SBS exhibit a pronounced heterogeneity, even at a low polymer concentration. For example, the binder modified with 3% radial SBS, Finaprene 411, has a continuous asphalt phase in which Finaprene 411 particles are coarsely dispersed (shown in Figure 7.33). A general distinction can be made between the binders with a continuous asphalt phase in which the polymer particles are dispersed, and the binders with a polymeric continuous phase in which asphalt globules are dispersed. Examples of photographs showing these two types of PMA morphology are presented in Figure 7.34 (binder modified with 5% radial SBS) and Figure 7.37 (binder modified with 5% linear SBS). The SBS phase appears light in color while the asphalt phase appears dark in color. The behavior of these two samples seems to be different with respect to the loss modulus, see Figure 7.29, and Figure 7.30. The sample of binder modified with 5% radial SBS exhibits a “more” elastic behavior than the sample modified by 5% linear SBS. Radial SBS, forms a lightly cross-linked network visible in Figure 7.33, which may be responsible for the presence of a local maximum of the loss tangent in the transition region. The network may exist in both the polymer-rich phase present as discrete particles (Figure 7.37, binder modified with 5% linear SBS), and the polymer-rich phase as continua (Figures 7.34 and 7.35, binder modified with 5% and 7% radial SBS).

The compatibility of polymer modified asphalts is the result of the mutual effects of polymer and asphalt, and consequently is mainly influenced by asphalt composition as well as polymer nature and content. As indicated in Figure 7.36 (binder modified with 3% linear SBS), there is no interaction among them at this low polymer concentration and a continuous polymer-rich phase may be obtained by increasing SBS concentration (Figure 7.38, binder modified with 7% linear SBS). The morphology of binders modified with SBS is also influenced by the characteristics of the SBS polymers. Compared to the binders modified with linear SBS, the binders modified with radial SBS show larger polymer domains, suggesting a lower degree of compatibility. This is probably caused

both by a difference in the polymer structure and its molecular weight. The radial SBS used in this work has higher molecular weight than the linear SBS, and an increased difference in molecular weight of the components may lead to lower compatibility of the system.

On the pictures which are shown, practically, in all cases, when SBS or SIS was used, materials with more than 5% polymers have probably dispersed asphalt in rubber. This might be the result of swallowing the oils from asphalt by rubber and thus the rubber/asphalt ratio is increased.

7.1.8.2 Binder Modified with SIS Polymer

Figure 7.39 shows the binder modified with 3% SIS, Kraton D1107, and the base asphalt. There is actually no difference between them. In this case, the mixture of 3% SIS polymer and the base asphalt is completely homogenous. It might be because the oils in the base asphalt completely solvate the Kraton D1107. With the increased concentration of Kraton D1107, continuous polymer-rich phases may be obtained for the binders modified with 5% and 7% SIS, Kraton D1107 (Figures 7.40 and 7.41). However by comparing the samples with 3%, and 5% of SIS, in the Figure 7.31 one can see that the ratio of the energy lost to the energy stored is decreasing with the increasing concentration of SIS, and for both of these concentrations this ration is much lower than for the base asphalt. It is true that no cross-linking is observed from Figure 7.31. The local maximum, at low reduced frequencies, for 3% sample indicates same structural changes. It is a question if such a behavior can be observed for the 5% concentration of SIS, at even lower reduced frequencies.

According to Van Beem and Brasser (1973), SBS and SIS belong to the thermoplastic rubbers, which consist of two-phase system with the polystyrene end blocks, associated in “domains” (Corbett, 1967), incorporated in a butadiene-or isoprene-rubber matrix in which they act as multifunctional cross-links. “On the polymer being dispersed in hot bitumen the polystyrene ‘domains’ weaken and may dissolve partly or

completely. Thus, SBS and SIS causes the blend to display viscous behavior at hot temperatures and at the same time, owing to the relatively low molecular weight of the individual SBS or SIS polymer molecules, effects only a moderate increase of the hot melt viscosity of the bitumen. Upon cooling the polystyrene blocks associate and once the temperature has dropped below their glass transition temperature (about 80 °C) they may serve as cross-links for the dispersed elastomer blocks. Provided that the elastomer mid-blocks remain well dispersed at ambient temperatures, a continuous rubber elastic network throughout the bitumen is obtained" (Van Beem and Brasser, 1973). *op. cit.* According to Kraus (1982), "elastomeric thermoplastic block polymers of butadiene and styrene are highly effective in converting asphalts into truly rubber-like materials." He also stated that a continuous rubber structure usually emerges at 6% to 8% polymer concentrations.

7.1.8.3 Binders Modified with EVA Polymers

As shown in Figures 7.42, 7.43, and 7.44, the binders modified with 3%, 5%, and 7% EVA polymer, Elvax 150W, none of them has a continuous polymer-rich phase. At a low polymer concentration of Elvax 150W, the binder modified with 3% Elvax 150W has a continuous asphalt phase in which Elvax 150W particles are finely dispersed. With the increased concentration of Elvax 150W, no connections among the Elvax 150W particles are observed. Same trend can be seen from the binders modified with 3% and 7% EVA, Elvax 350, as illustrated in Figures 7.45, and 7.47, with the exception for the binder modified with 5% Elvax 350. The Figure 7.23 reveals almost no crosslinking (only very weak local maxima, for 3% and 5% Elvax 350, in the transition zone), however the decrease of the loss tangent (at low reduced frequencies) with the increase of concentration, and the low values of this function point to the structural changes leading to a weak crystalline-like structure of these materials.

The viscoelastic properties of a binder modified with polymers are influenced by the morphology of the system. For example, the binder modified with SBS with a continuous polymer-rich phase (Figure 7.34, and 7.37) can behave like a crosslinked

rubber and display rubber-like elasticity, while binders modified with discrete small polymer particles in principle behave like unmodified asphalts.

Despite some evidence showed that the degree of compatibility affect the rheological properties of the binders modified with polymers, it is still very difficult to establish a quantitative relationship between PMA compatibility defined by its microstructure, and rheological properties.

7.2 Glass Transition Temperature

The glass transition temperature (T_g) is the temperature at which amorphous substance changes from a glassy state to fluid condition (Schmidt, 1966). Below T_g , material becomes brittle and glass-like without plastic flow (Schmidt et al. 1965). A brief introduction to the glass transition temperature problem is discussed in section 2.3.1.4. The measurement of the glass transition temperatures is affected by several factors, which will be discussed below.

7.2.1 The Procedure of Dynamic Mechanical Analysis

In this thesis, the dynamic mechanical analysis (DMA) was used for the estimation of the glass transition temperature, T_g . In the dynamic mechanical experiment a known sinusoidal strain is applied to the different polymer modified asphalt and regular asphalt samples and both, the phase shift and the magnitude of the resulting stress are measured. The Bohlin (VOR) rheometer, which is a controlled strain rheometer, was used to measure the glass transition temperature from the loss modulus, G'' , in this study.

All the measurements were made in the linear viscoelastic region. For the study of T_g , only two frequencies were chosen, 0.1Hz and 1Hz, the investigated temperature range was $-40\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$.

There are several important factors that might affect the test results.

Gap setting

The gap setting is a very important factor for the parallel plate geometry. The gap height is generally in a range between 0.9 to 2.5 mm, depending on the temperature. Large gap is used for the low temperatures and the small gap is used for the high temperature experiments.

Plate size

The plate diameter varies, depending on the stiffness of the sample and the operating temperature. For majority of polymer modified asphalt binders, the following plates were used:

Temperature	Plate diameter
$T \geq 50\text{ }^{\circ}\text{C}$	30.0 mm
$30\text{ }^{\circ}\text{C} \leq T < 50\text{ }^{\circ}\text{C}$	25.0 mm
$0\text{ }^{\circ}\text{C} \leq T < 30\text{ }^{\circ}\text{C}$	8.0 mm
$-40\text{ }^{\circ}\text{C} \leq T < 0\text{ }^{\circ}\text{C}$	6.0 mm

When asphalt is measured at low temperatures, grooved plates could be used to avoid slip. Special care must be taken to ensure the parallelism of the plates. In my study, all the plates used were the smooth plates.

Amplitude

Determining the amplitude (strain level) is crucial for linear viscoelastic measurements. The strain level has to be made within the linear viscoelastic region. With the temperature increasing, the amplitude can be increased.

Frequency

The behavior of asphalt samples is generally non-Newtonian at high oscillatory frequencies (Billiter et al., 1995). However, a limiting Newtonian behaviour is usually

obtained at low frequency using the time-temperature superposition principle (Ferry, 1985). Therefore, the frequency should be carefully chosen, and one has to assure that the measurements are done in the linear viscoelastic region, i.e., the material functions (e.g., G' , G'') are independent of the applied strain levels.

Temperature

Since the transducer of rheometer is not infinitely stiff, the instrument gives correct data only over a very limited range at low temperature. This problem may limit the accessible temperature range of the measurement.

7.2.2 Glass Transition Temperature from Dynamic Mechanical Analysis

Wada and Hirose (1960) reported that the asphalt is viscoelastic above T_g , and that the maximum of the loss modulus occurs in the T_g region. We assume that the loss modulus, as a function of temperature, attains its maximum at the glass transition temperature, T_g . It was found that the glass transition temperatures of the studied binders, modified with polymers, depend on the frequency of the used harmonic deformation. The measured $G''(T; \nu)$, where ν represents the frequency in Hz, have been fitted to the peak function from which the position of the maximum of $G''(T; \nu)$ can be estimated. The results of this procedure are presented in Table 7.11, and the detailed discussion follows.

Table 7.11 Glass Transition Temperature at 0.1 Hz and 1 Hz

Sample Composition	T_g [K], ($^{\circ}\text{C}$)	T_g [K], ($^{\circ}\text{C}$)
	(Frequency=0.1 Hz)	(Frequency=1 Hz)
200/300 & 5% radial SBS (Finaprene 411)	244 (-29)	250 (-23)
200/300 & 5% linear SBS (Kraton D1102)	242 (-31)	248 (-25)
200/300 & 5% EVA (Elvax 350)	242 (-31)	247 (-26)
200/300 base asphalt	245 (-28)	248 (-25)

7.2.2.1 Glass Transition Temperature at 0.1 Hz

7.2.2.1.1 Base Asphalt

Figure 7.48 presents G' , and G'' of the base asphalt at different temperatures and the fixed frequency of 0.1 Hz. When the temperatures are higher than 263 K, G'' is greater than G' . When the temperatures are lower than 263 K, G'' becomes smaller than G' while G' increases continuously and slowly. There is an apparent peak of G'' in the interval of temperatures 233 K to 253 K.

The peak of G'' is estimated from the fit of $G''(T; \nu)$ to the peak function shown in Figure 7.49. The estimated peak temperature is 245 K.

7.2.2.1.2 Asphalt Modified by SBS Polymers

Figure 7.50 shows G' , and G'' of the binder modified with 5% radial SBS (Finaprene 411) at different temperatures for frequency 0.1 Hz. When the temperatures are higher than 253 K, G'' is greater than G' . When the temperatures are lower than 253 K, G'' becomes lower than G' , and attains a maximum in the region 243 K to 253 K, while G' still increases.

By fitting the function $G''(T; \nu)$ to the peak function shown in Figure 7.51, the glass transition temperature is estimated at 244 K.

Figure 7.52 presents G' , and G'' of the binder modified with 5% linear SBS (Kraton D1102) as the function of temperature, for frequency 0.1 Hz. When the temperatures are higher than 273 K, G'' is greater than G' . When the temperatures are lower than 273 K, G'' becomes lower than G' , and a peak is formed between 233 K to 253 K, while G' still has a tendency to increase.

The peak of G'' is obtained from the peak function shown in Figure 7.53. The estimated peak temperature is 242 K.

7.2.2.1.3 Asphalt Modified by EVA Polymers

Figure 7.54 shows G' , and G'' of the binder modified with 5% EVA (Elvax 350) at different temperatures and the fixed frequency of 0.1 Hz. When the temperatures are higher than 263 K, G'' is greater than G' . When the temperatures are lower than 263 K, G'' becomes lower than G' while G' still increases linearly. In Figure 7.54, no peak is resolved on the curve G'' since the measurements at lower temperatures are beyond the instrument's limit.

By fitting the loss modulus to a peak function, Figure 7.55, the peak temperature is estimated as $T = 242$ K.

7.2.2.2 Glass Transition Temperature at 1 Hz

The procedure of obtaining the glass transition temperature at frequency 1 Hz is same as that for the frequency, $\nu = 0.1$ Hz.

7.2.2.2.1 Base Asphalt

Figure 7.56 shows G' , and G'' of the base asphalt at different temperatures and the fixed frequency of 1 Hz. The peak of G'' is estimated from the fit of $G''(T; \nu)$ to the peak function shown in Figure 7.57. The estimated peak temperature is 248 K.

7.2.2.2.2 Asphalt Modified by SBS Polymers

Figure 7.58 shows G' , and G'' of the binder modified with 5% radial SBS (Finaprene 411) at different temperatures and the fixed frequency of 1 Hz. In this figure, it is observed that when the temperature is higher than 273 K, G'' becomes smaller than G' , and a peak is formed between 243K to 263K, while G' still has a tendency to increase.

By fitting the function $G''(T; \nu)$ to the peak function shown in Figure 7.59, the glass transition temperature is estimated at 250 K.

Figure 7.60 shows G' and G'' of the binder modified with 5% linear SBS (Kraton D1102) at different temperatures for the fixed frequency of 1 Hz. The peak of G'' is obtained from the peak function shown in Figure 7.61. The estimated peak temperature is 248 K.

7.2.2.2.3 Asphalt Modified by EVA Polymers

Figure 7.62 shows G' , and G'' of the binder modified with 5% EVA (Elvax 350) at different temperatures for the frequency of 1 Hz. When the temperatures are higher than 273 K, G'' is greater than G' . When the temperatures are lower than 273 K, G'' becomes smaller than G' while G' still increases linearly. In the figure, no peak is obvious on the curve G'' .

The peak of G'' is estimated from fit to the peak function shown in Figure 7.63. The estimated peak temperature is 247 K.

It is found, from the Table 7.11, that the lower testing frequency yields the lower glass transition temperature. At frequency 0.1 Hz, the binders modified with polymers have lower glass transition temperatures than the base asphalt, and at the test frequency of 1 Hz, the estimated glass transition temperatures of the base asphalt and the modified samples are basically the same. Generally the lower frequencies of oscillations can excite the “heavier” structural units of the tested material. Thus it seems natural that at frequency of 1 Hz, one does not see the difference in T_g of the base and the modified binders. At frequency 0.1 Hz some structural units of the modified samples (units present due to the interactions between the base and the modifying polymers) are excited and thus the difference in T_g of the base and the modified samples is more pronounced. The frequency of 1 Hz is applied in most of the DMA data used for the determination of T_g . However the comparisons of dynamic mechanical data with the differential scanning calorimetry data suggest that frequencies between 0.01 and 0.1 Hz most closely match the DSC midpoint value recorded at less than 20 K/min (Selyer, 1994). It is recognized that the glass transition is better characterized by an interval of temperatures rather than

one singular temperature called T_g

Thus the performed DMA measurements can serve only as an estimate of the glass transition temperature “region” for the studied bituminous systems.

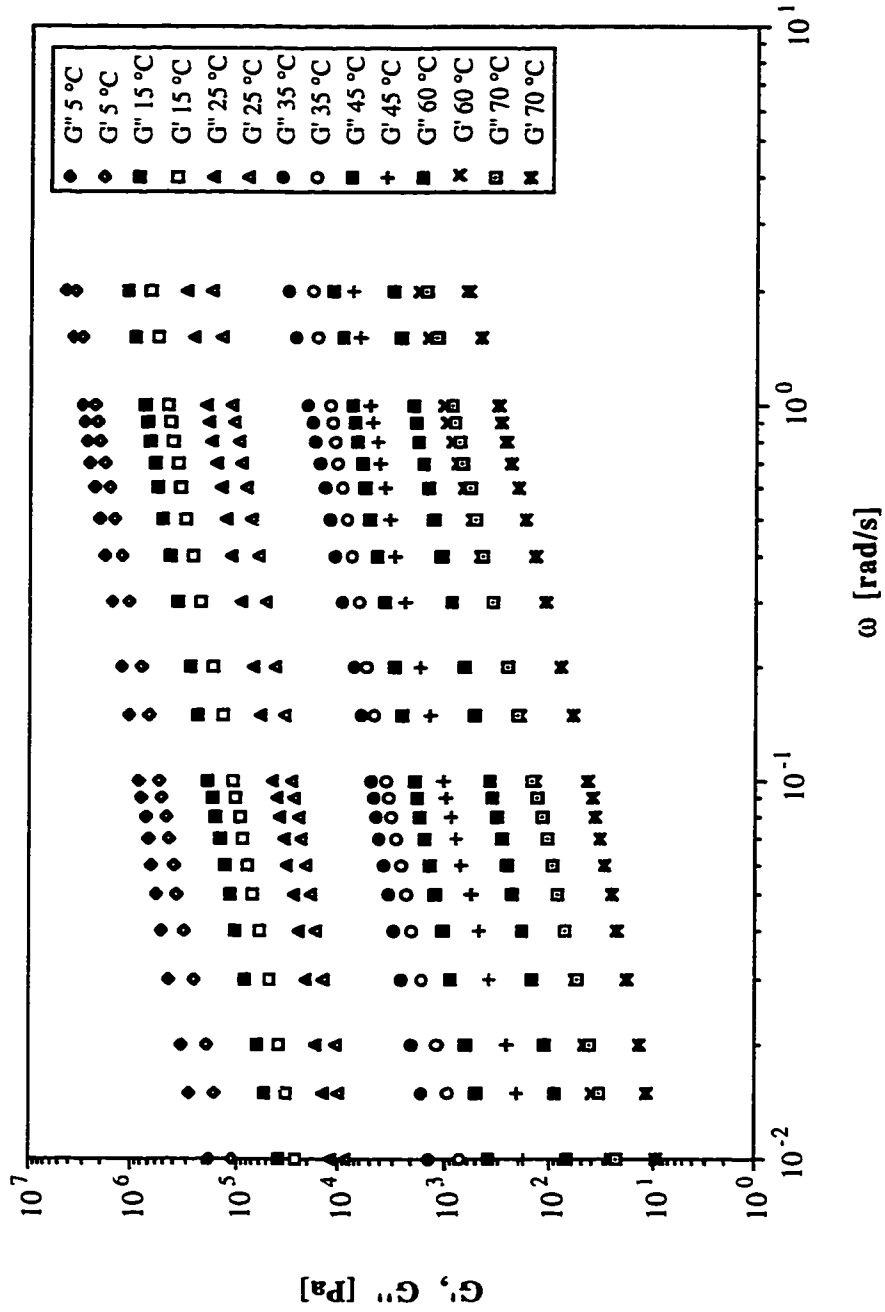


Figure 7.1 Dynamic Material Functions for Binder Modified with 5% Radial SBS

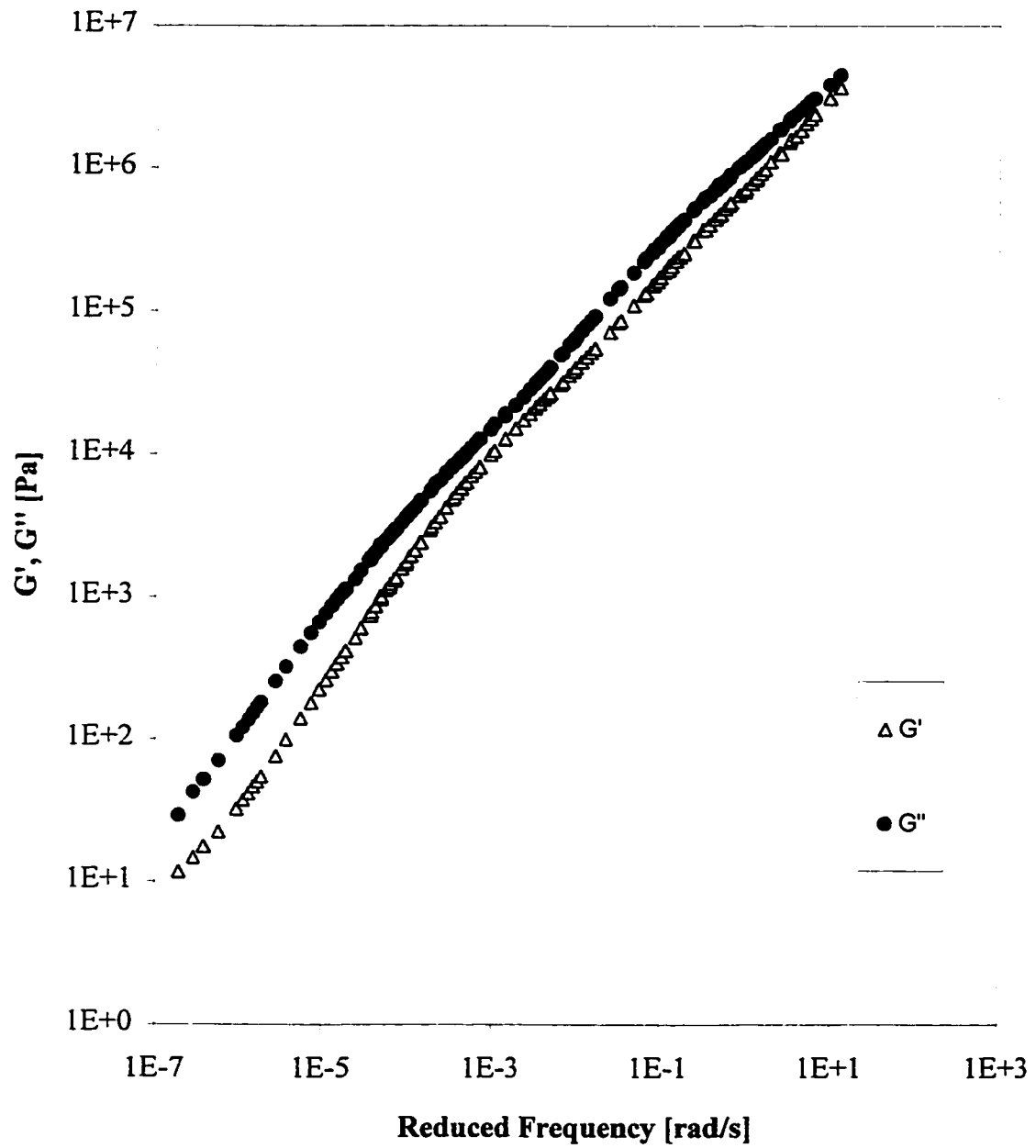


Figure 7.2 Master Curves of Binder Modified with 5% Radial SBS at Reference Temperature 5°C

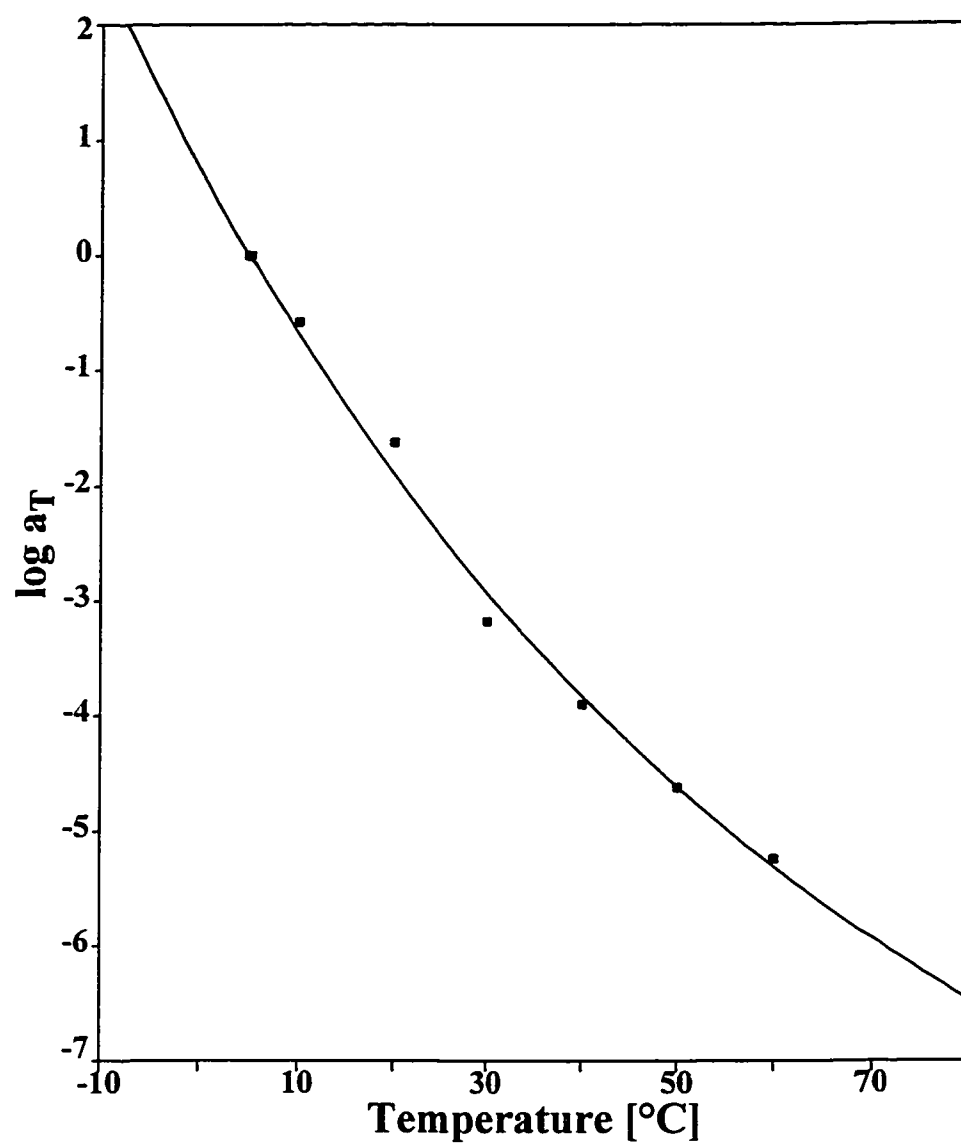


Figure 7.3 Shift Factor for Binder Modified with 5% Radial SBS at Reference Temperature 5 °C

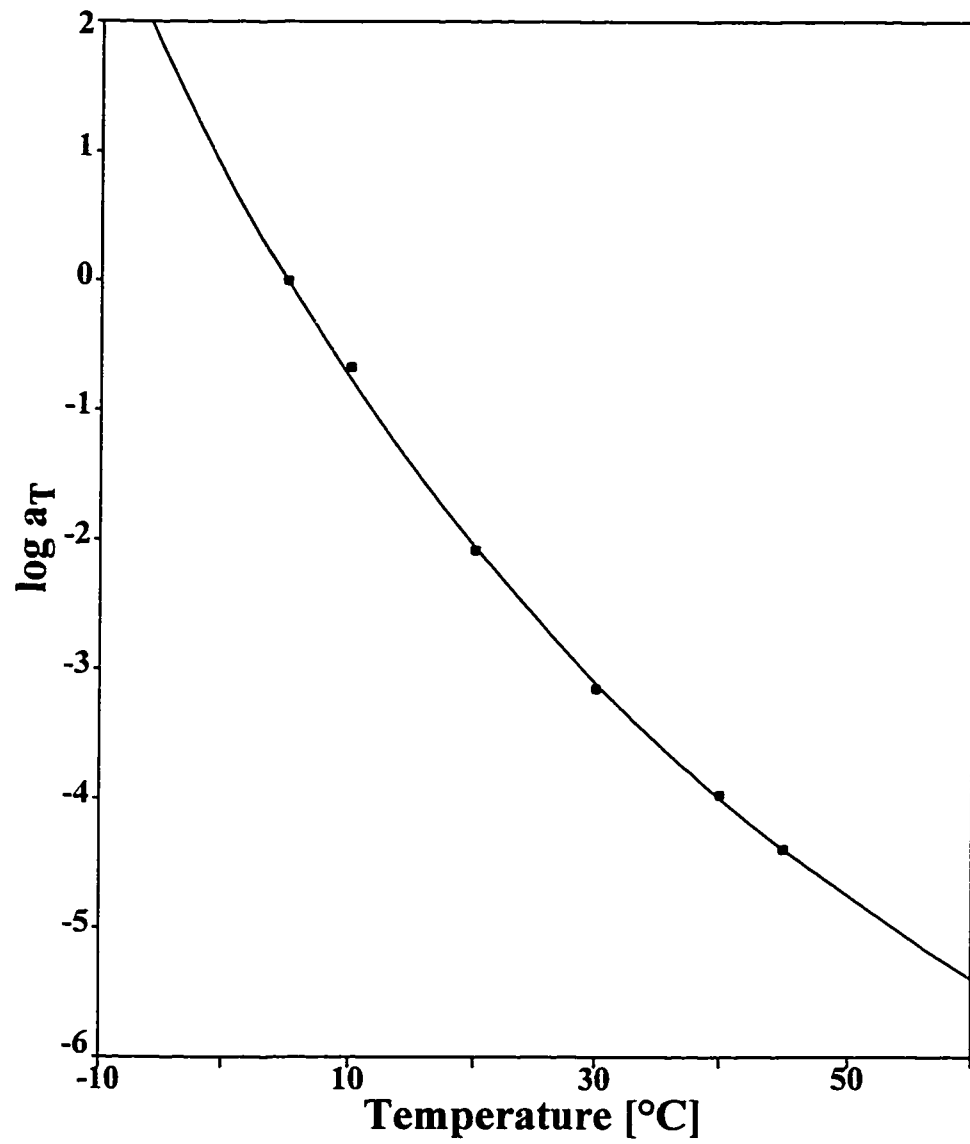


Figure 7.4 Shift Factor for Base Asphalt at Reference Temperature 5 $^{\circ}\text{C}$

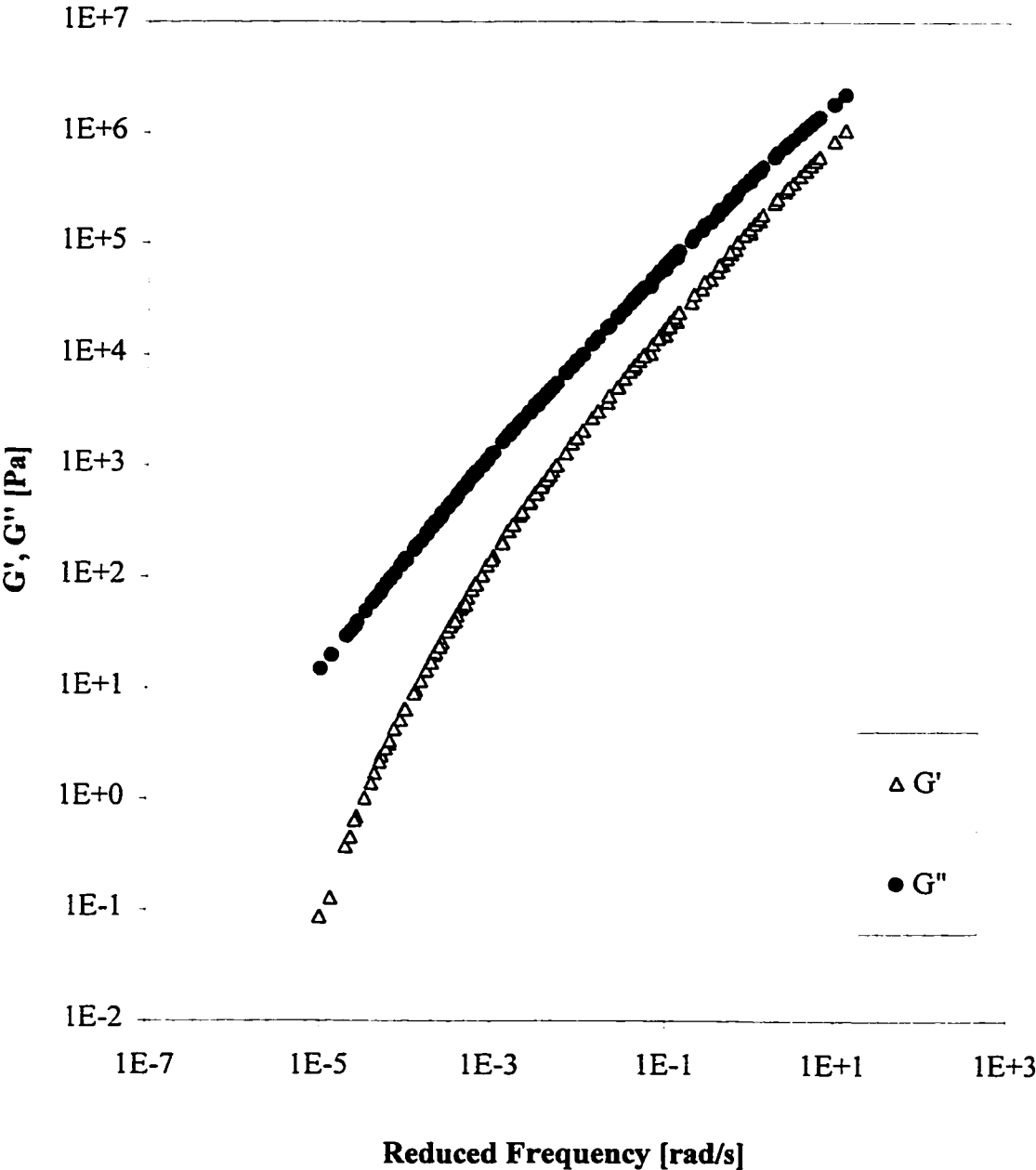


Figure 7.5 Master Curves of Base Asphalt at Reference Temperature 5°C

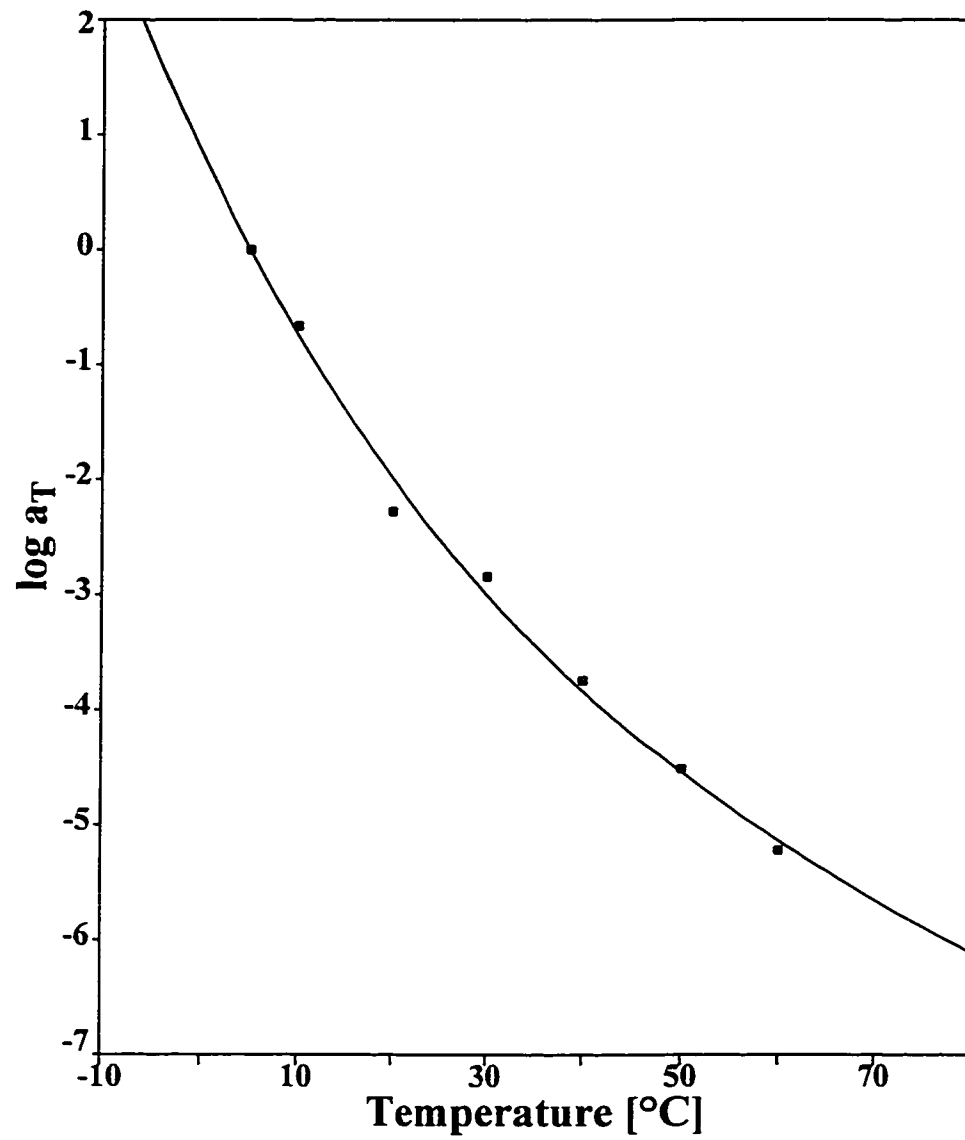


Figure 7.6 Shift Factor for Binder Modified with 3% Radial SBS at Reference Temperature 5 $^{\circ}\text{C}$

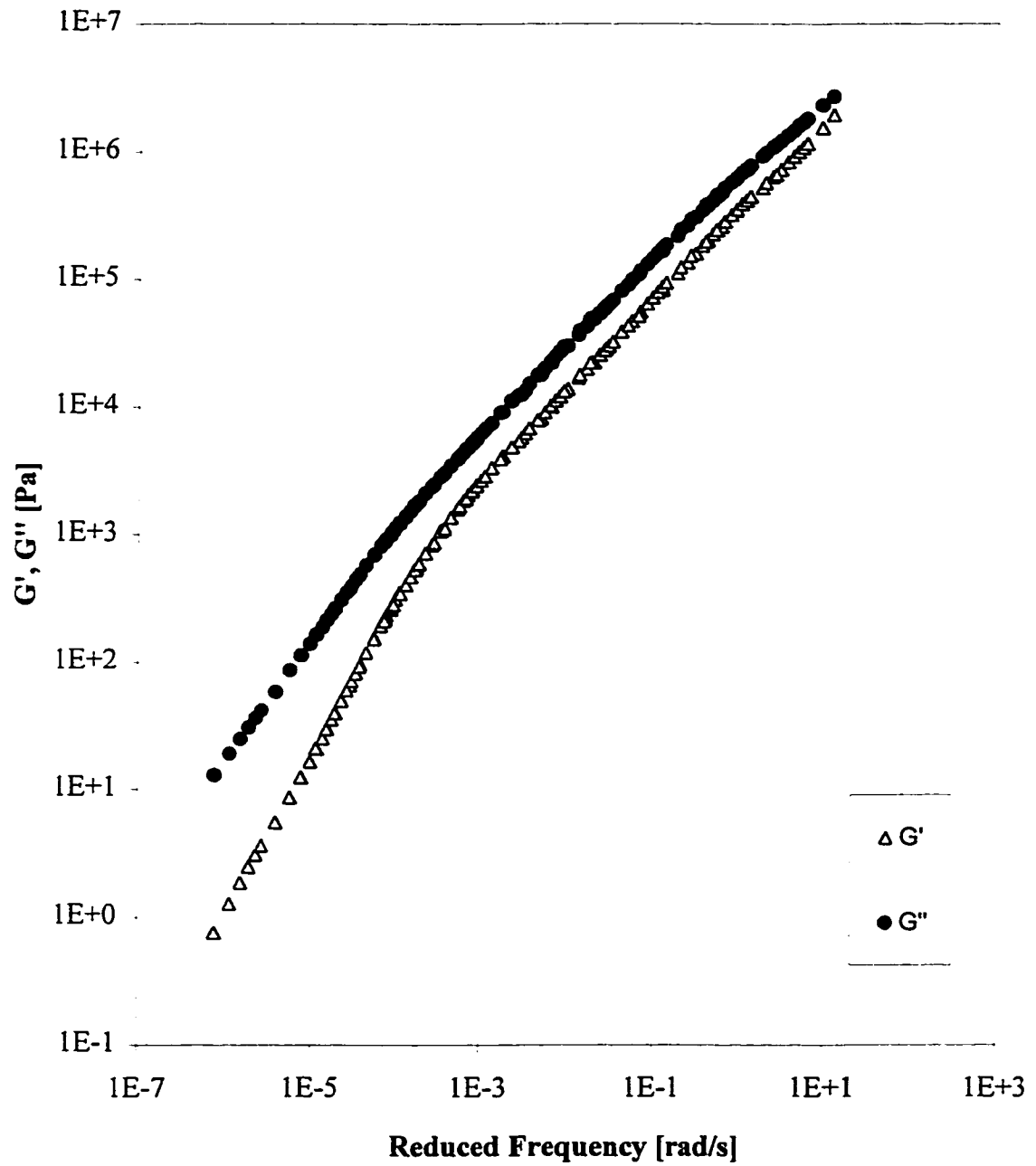


Figure 7.7 Master Curves of Binder Modified with 3% Radial SBS at Reference Temperature 5°C

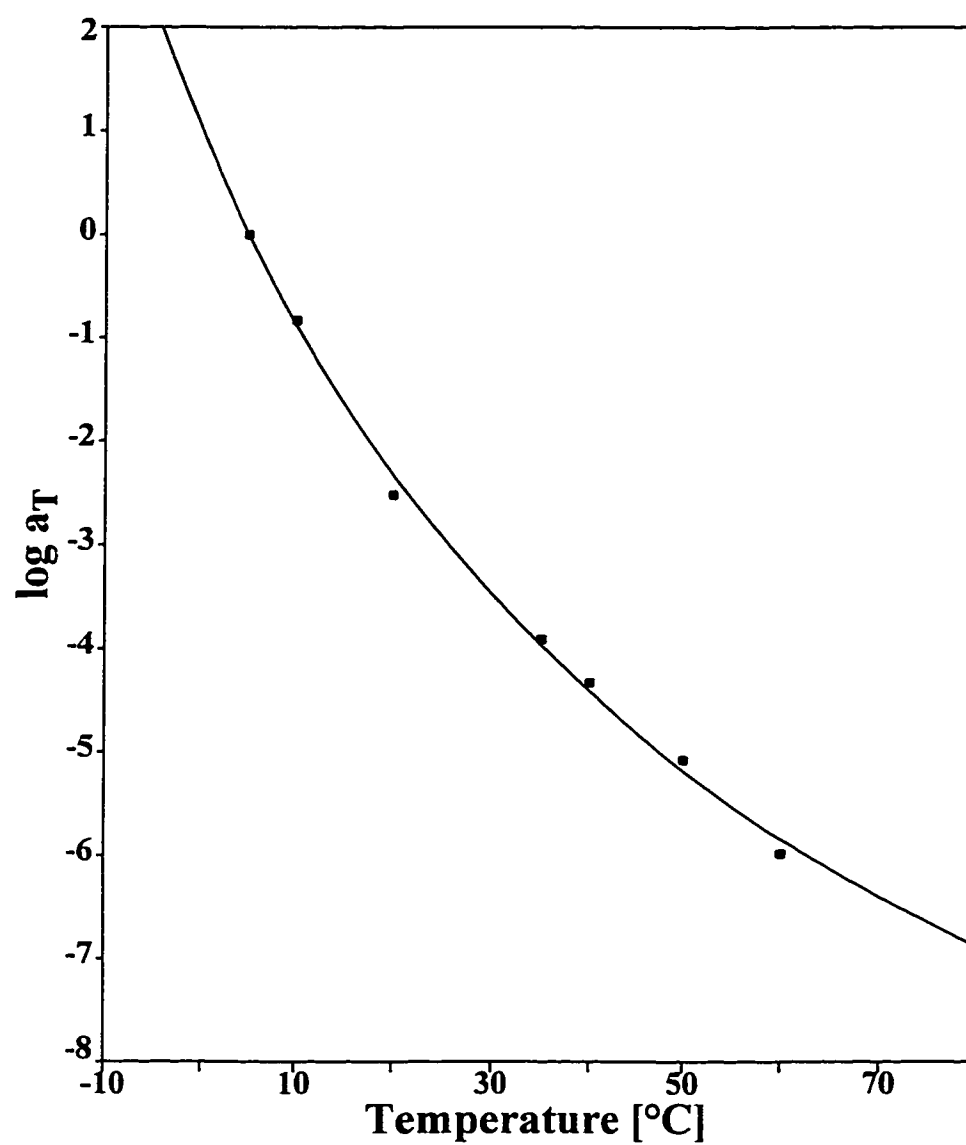


Figure 7.8 Shift Factor for Binder Modified with 3% Linear SBS at Reference Temperature 5 °C

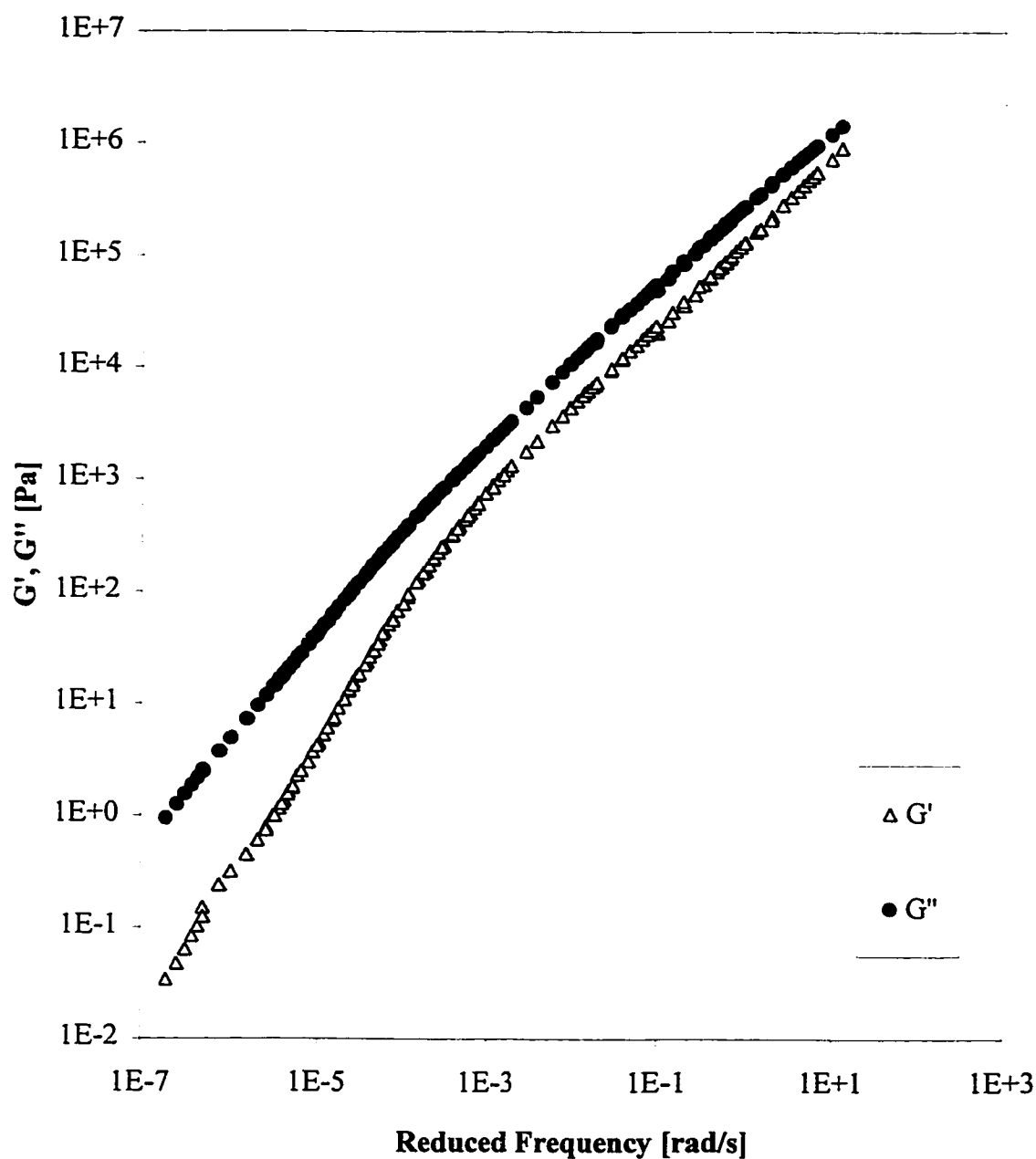


Figure 7.9 Master Curves of Binder Modified with 3% Linear SBS at Reference Temperature 5°C

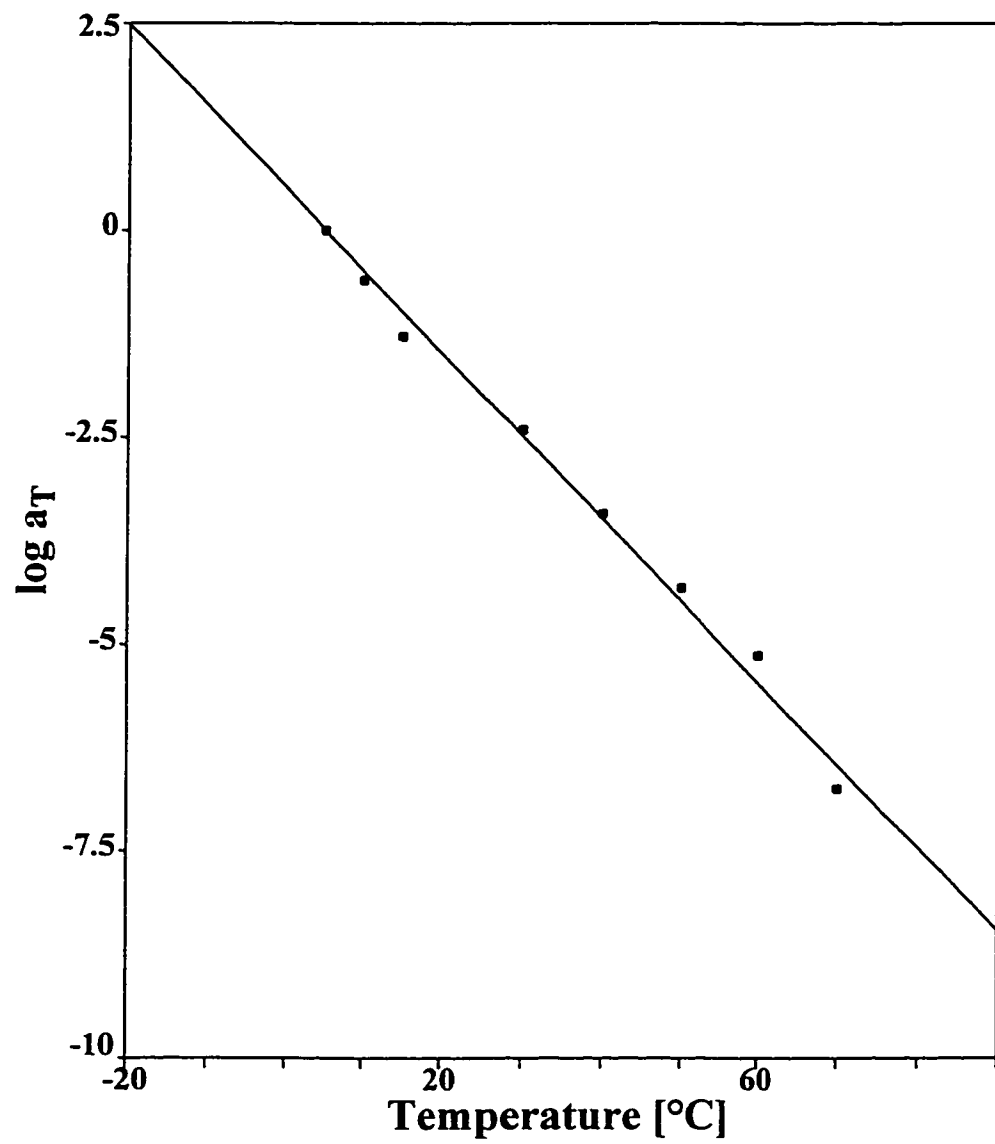


Figure 7.10 Shift Factor for Binder Modified with 5% Linear SBS at Reference Temperature 5 °C

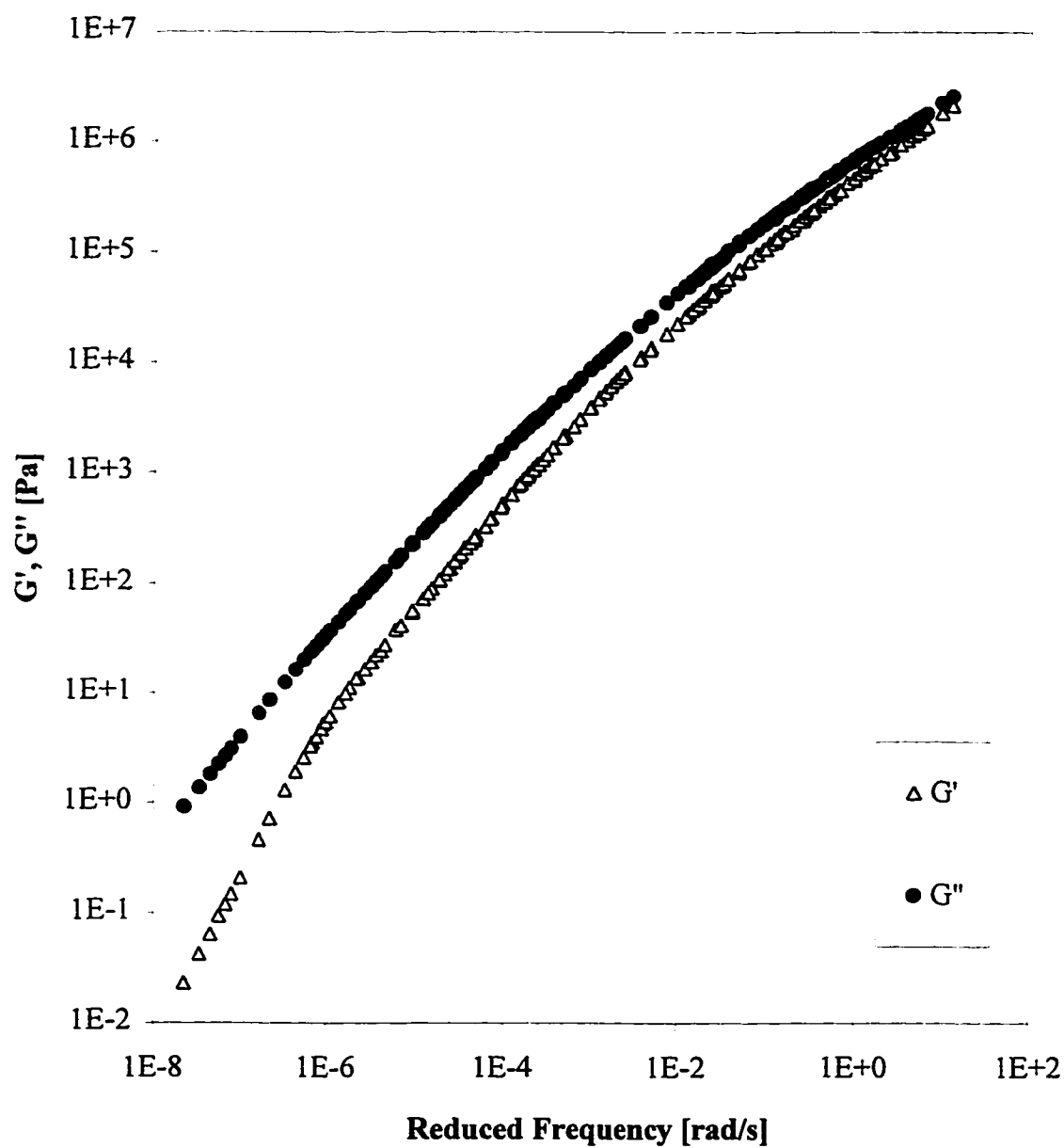


Figure 7.11 Master Curves of Binder Modified with 5% Linear SBS at Reference Temperature 5°C

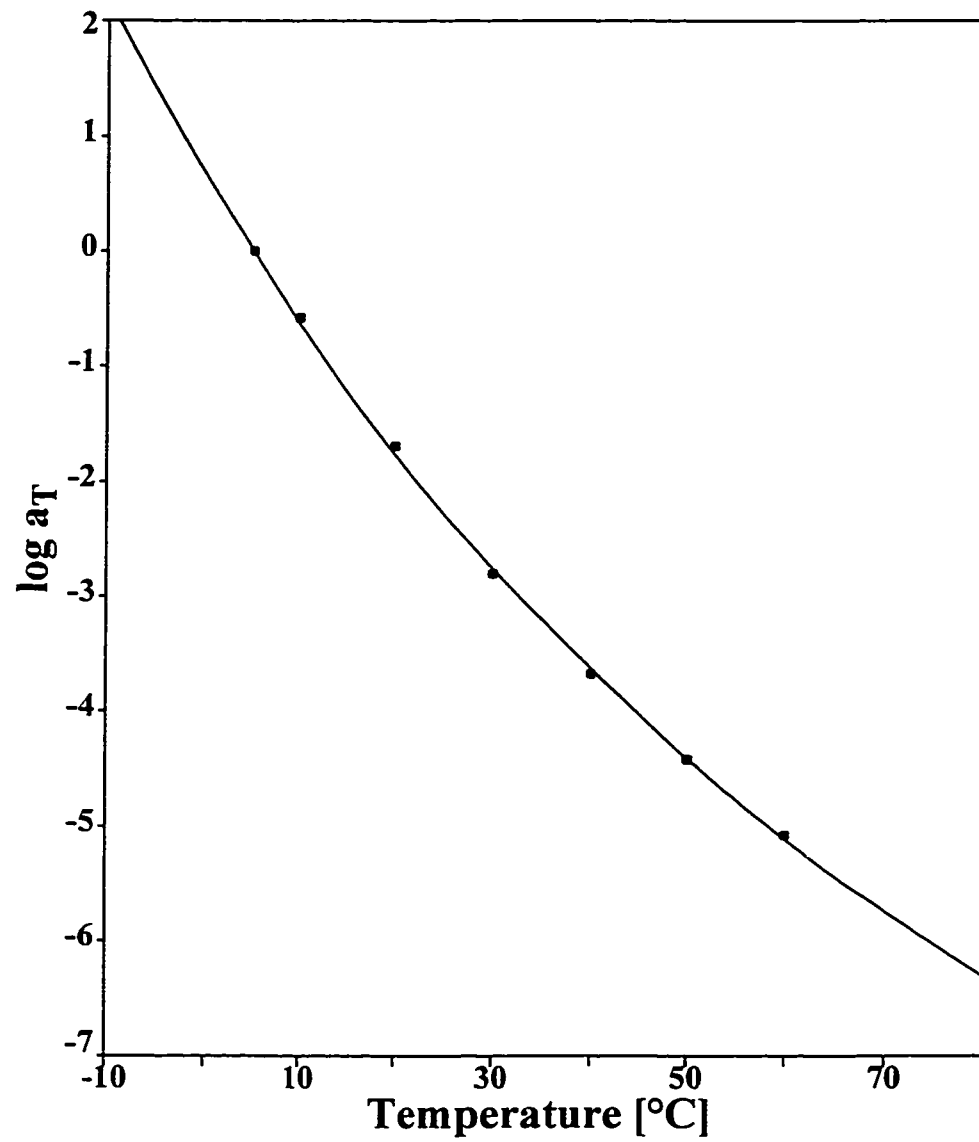


Figure 7.12 Shift Factor for Binder Modified with 3% Linear SIS at Reference Temperature 5 °C

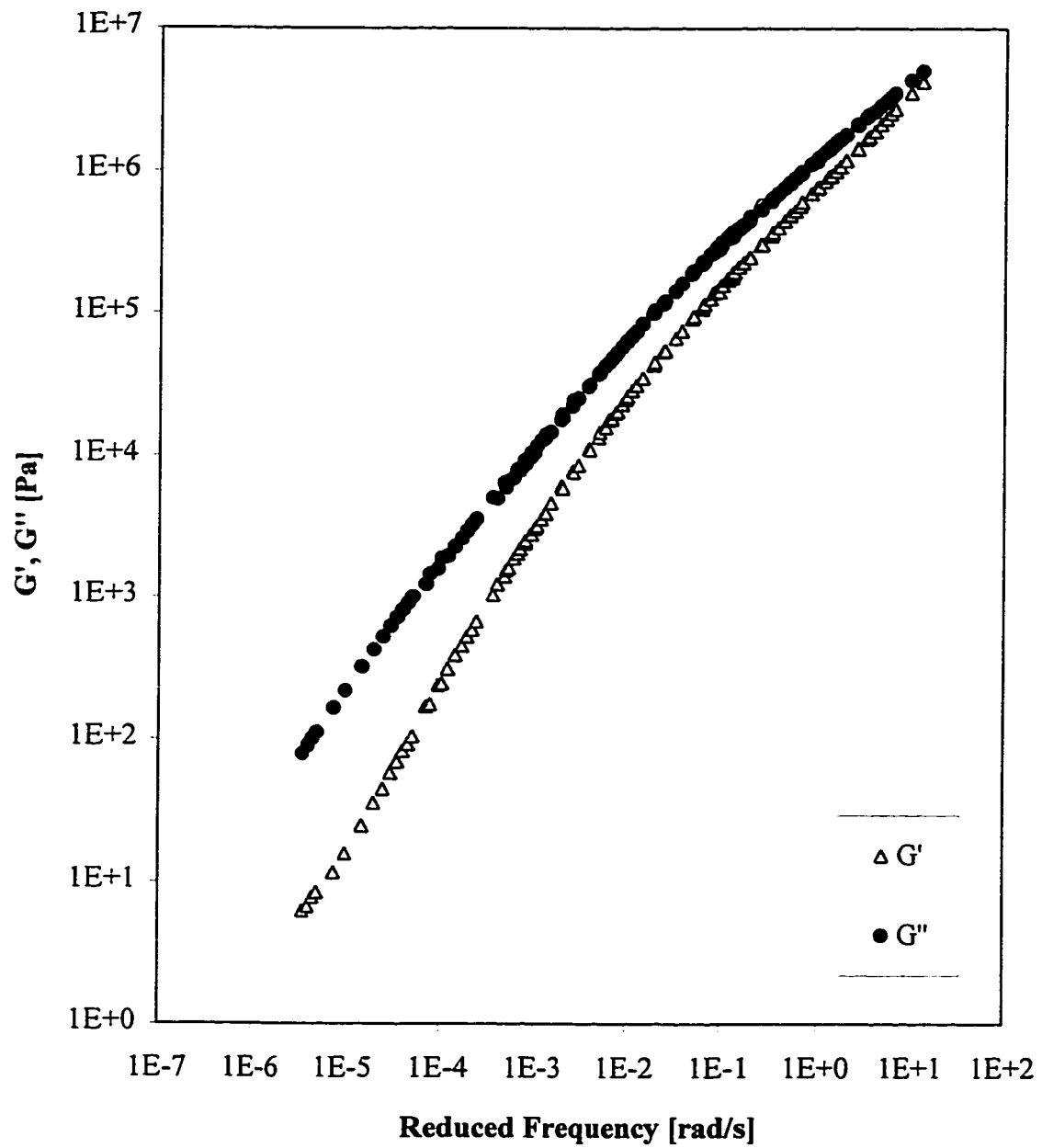


Figure 7.13 Master Curves of Binder Modified with 3% Linear SIS at Reference Temperature 5 °C

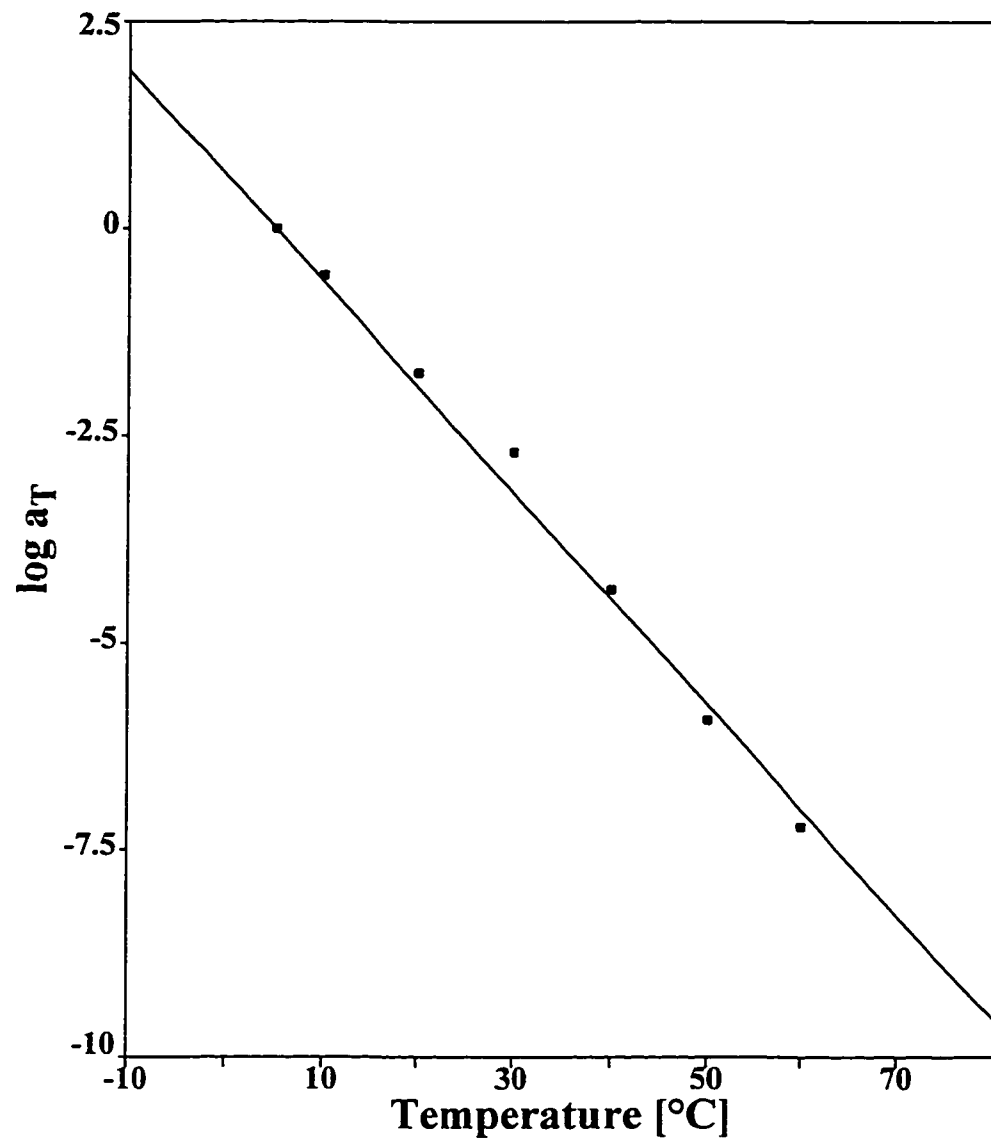


Figure 7.14 Shift Factor for Binder Modified with 5% Linear SIS at Reference Temperature 5 °C

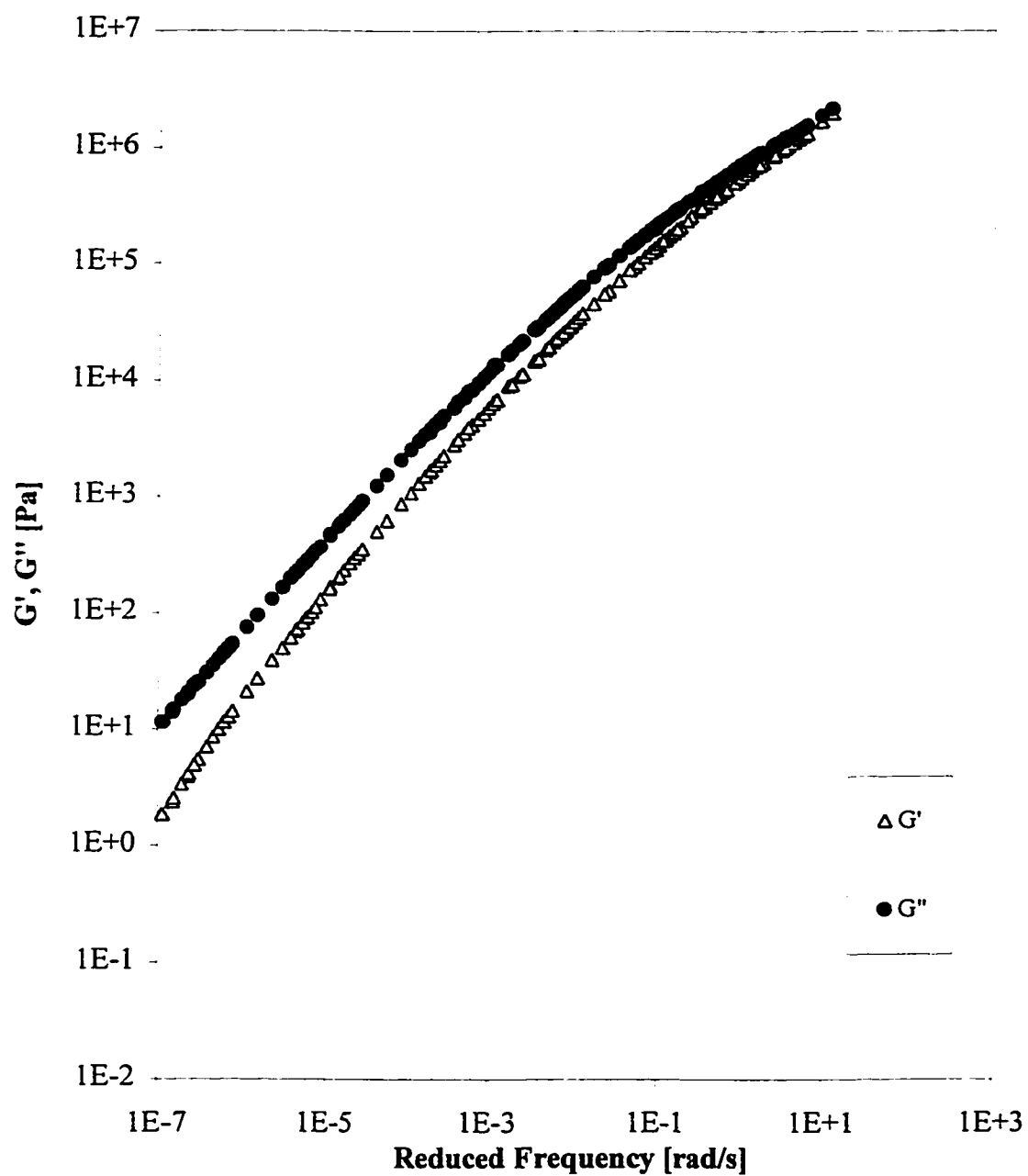


Figure 7.15 Master Curves of Binder Modified with 5% Linear SIS at Reference Temperature 5°C

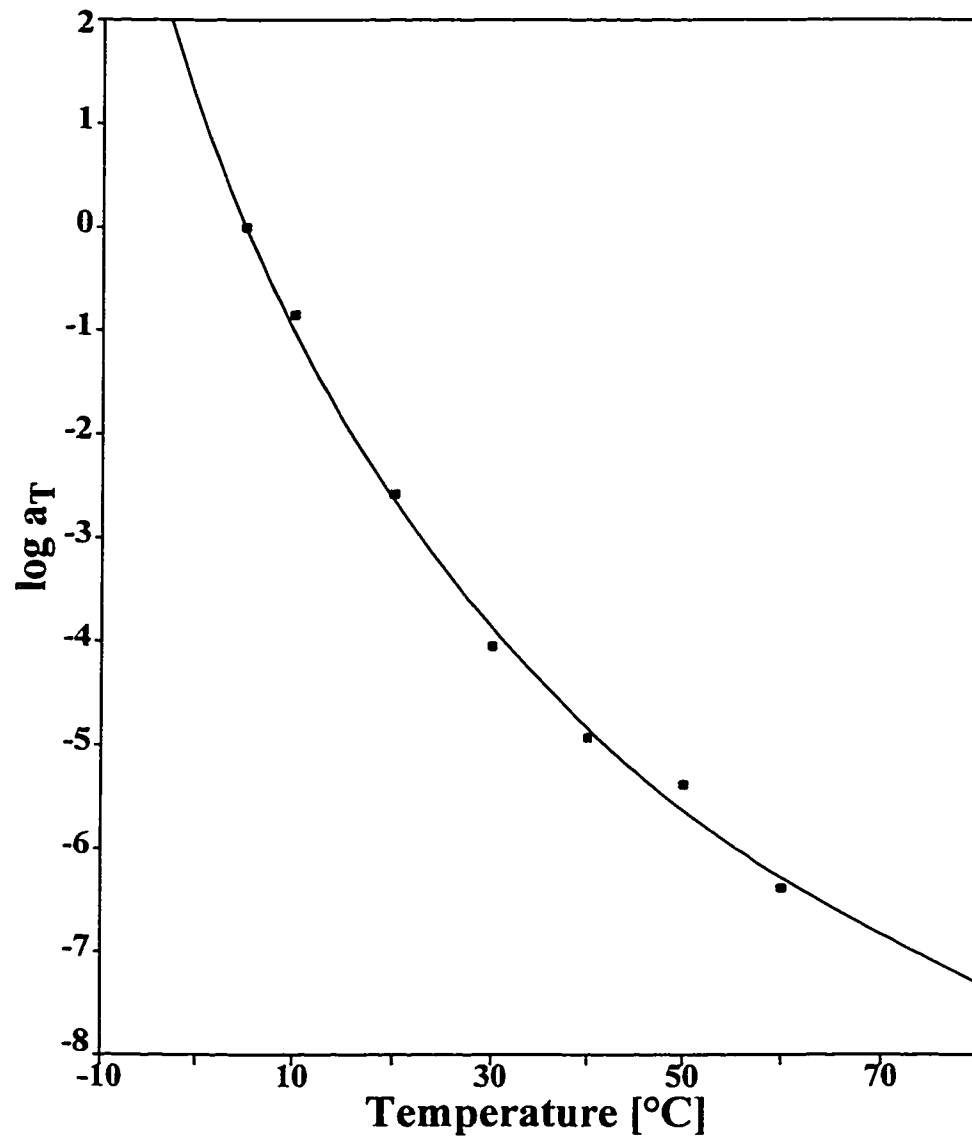


Figure 7.16 Shift Factor for Binder Modified with 3% EVA (Elvax 350) at Reference Temperature 5 °C

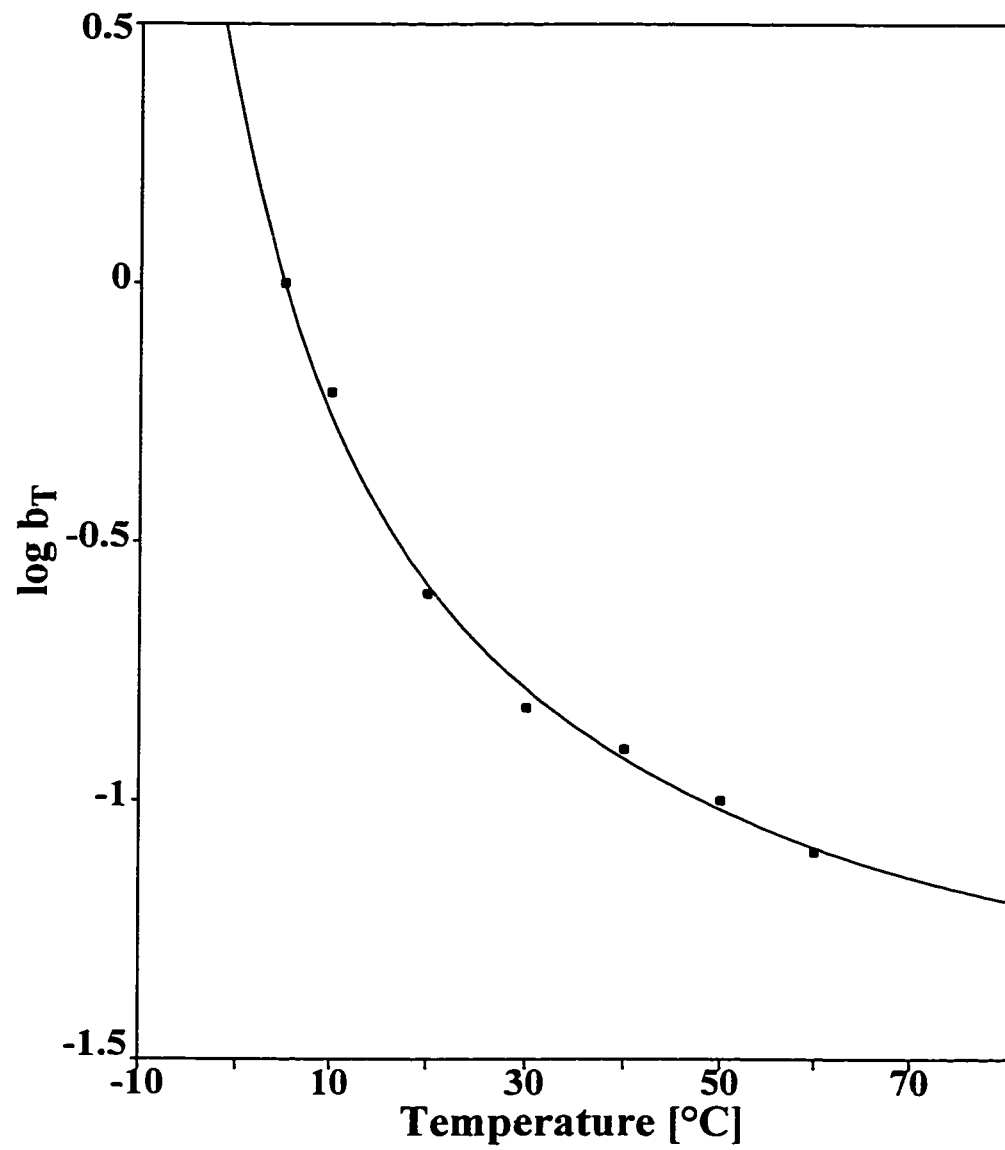


Figure 7.17 Shift Factor for Binder Modified with 3% EVA (Elvax 350) at Reference Temperature 5 °C (Vertical Shift)

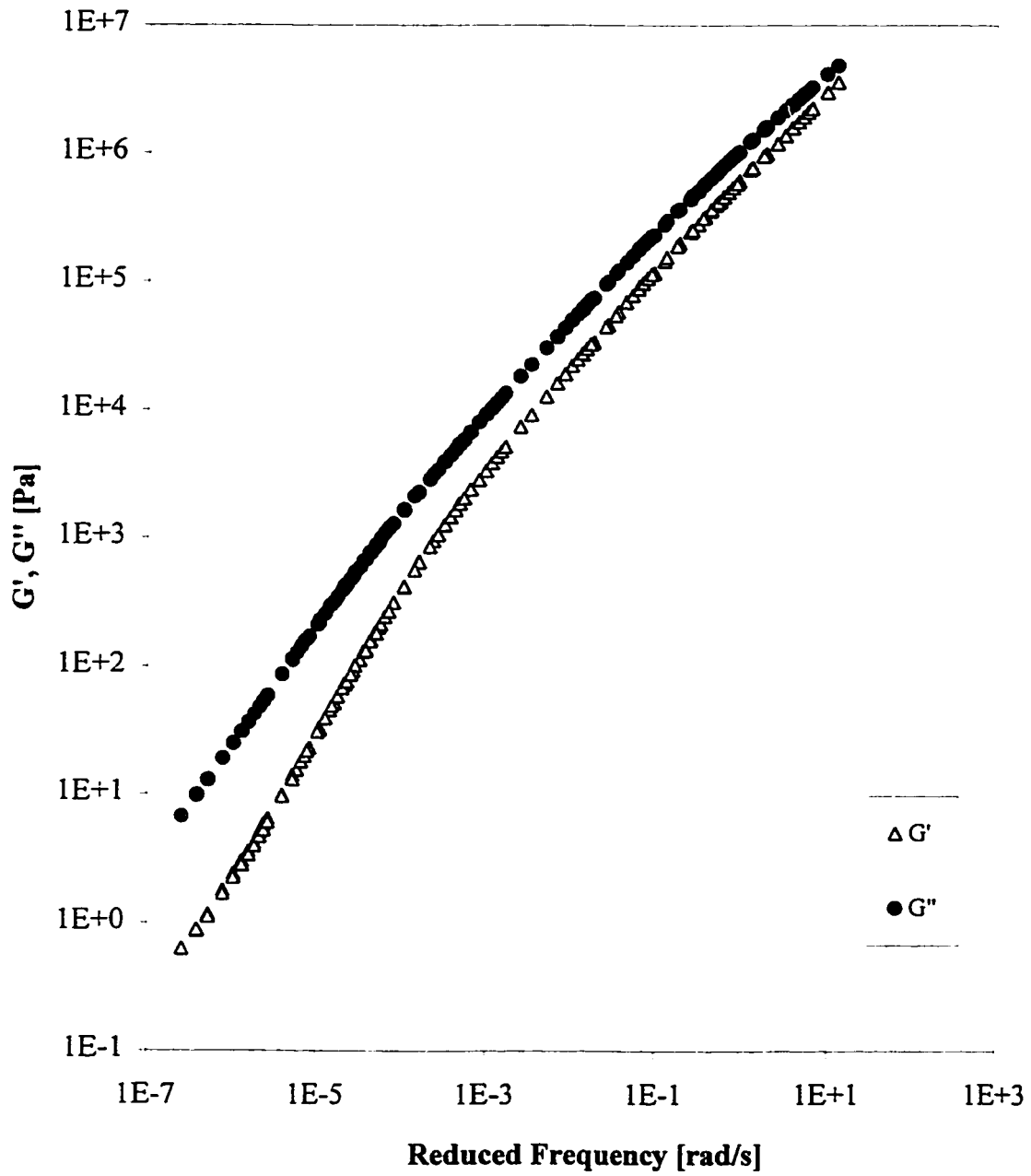


Figure 7.18 Master Curves of Binder Modified with 3% EVA (Elvax 350) at Reference Temperature 5°C

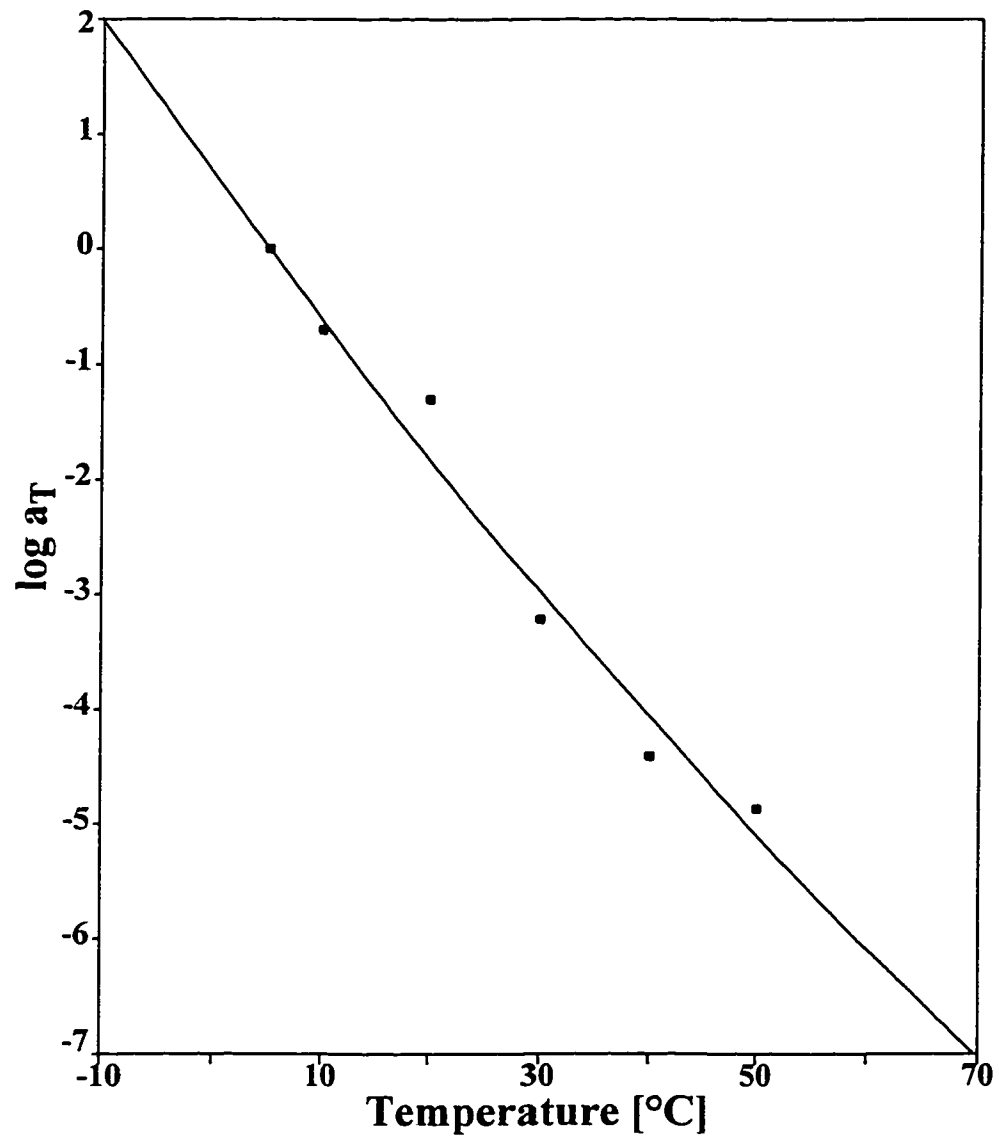


Figure 7.19 Shift Factor for Binder Modified with 5% EVA (Elvax 350) at Reference Temperature 5 °C

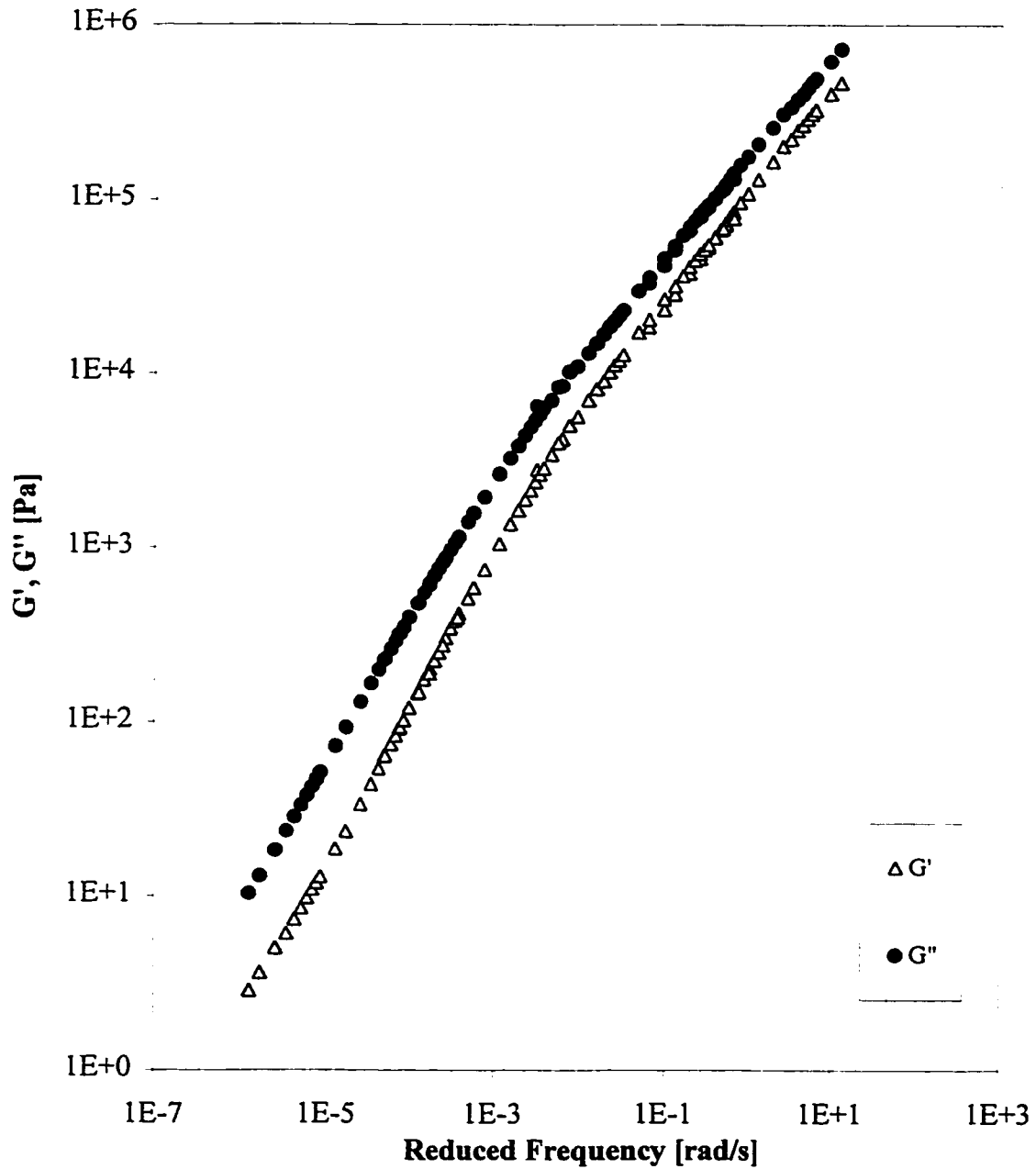


Figure 7.20 Master Curves of Binder Modified with 5% EVA (Elvax 350) at Reference Temperature 5°C

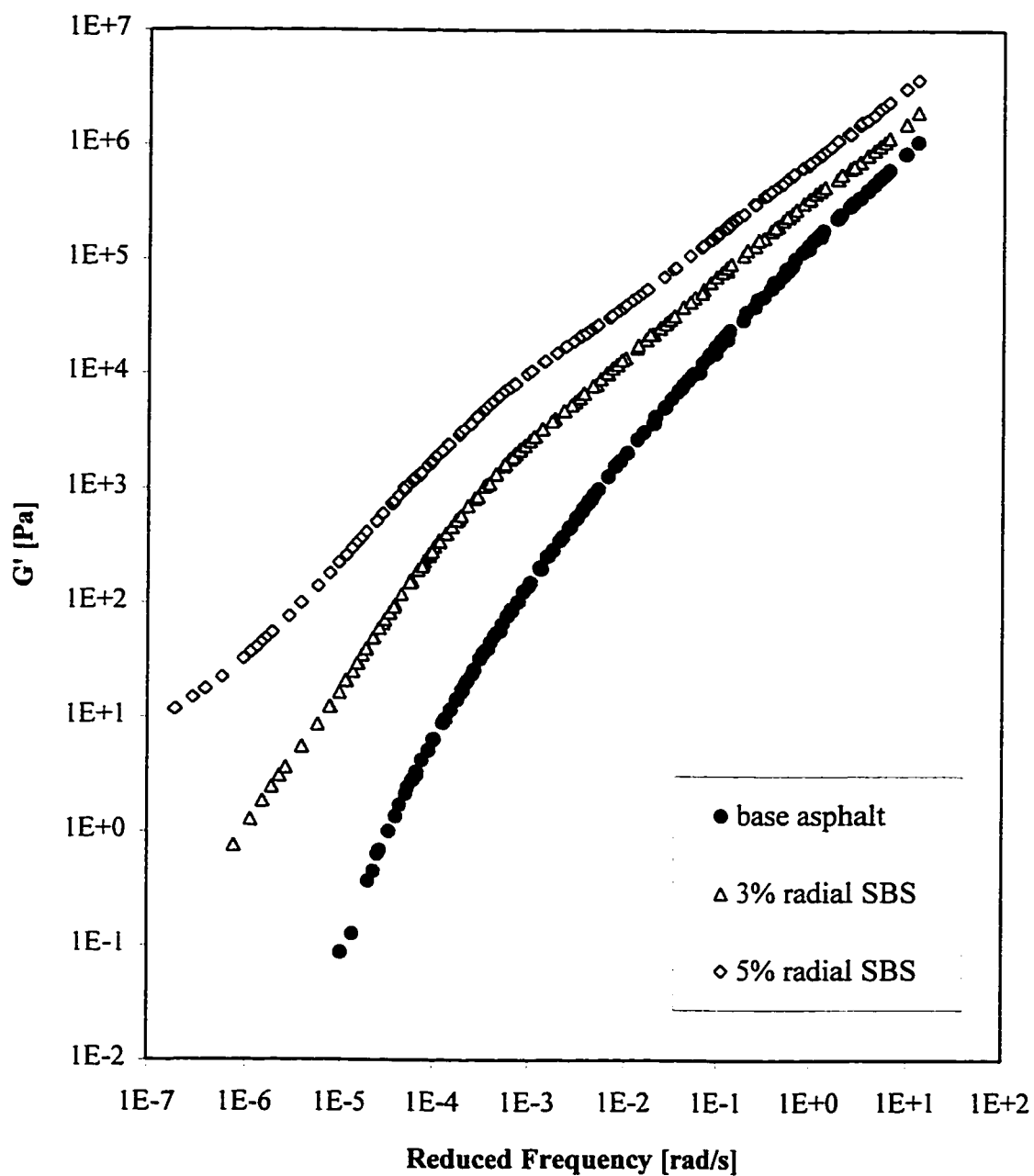


Figure 7.21 G' of Different Concentrations of Binders Modified with Radial SBS at Reference Temperature 5°C

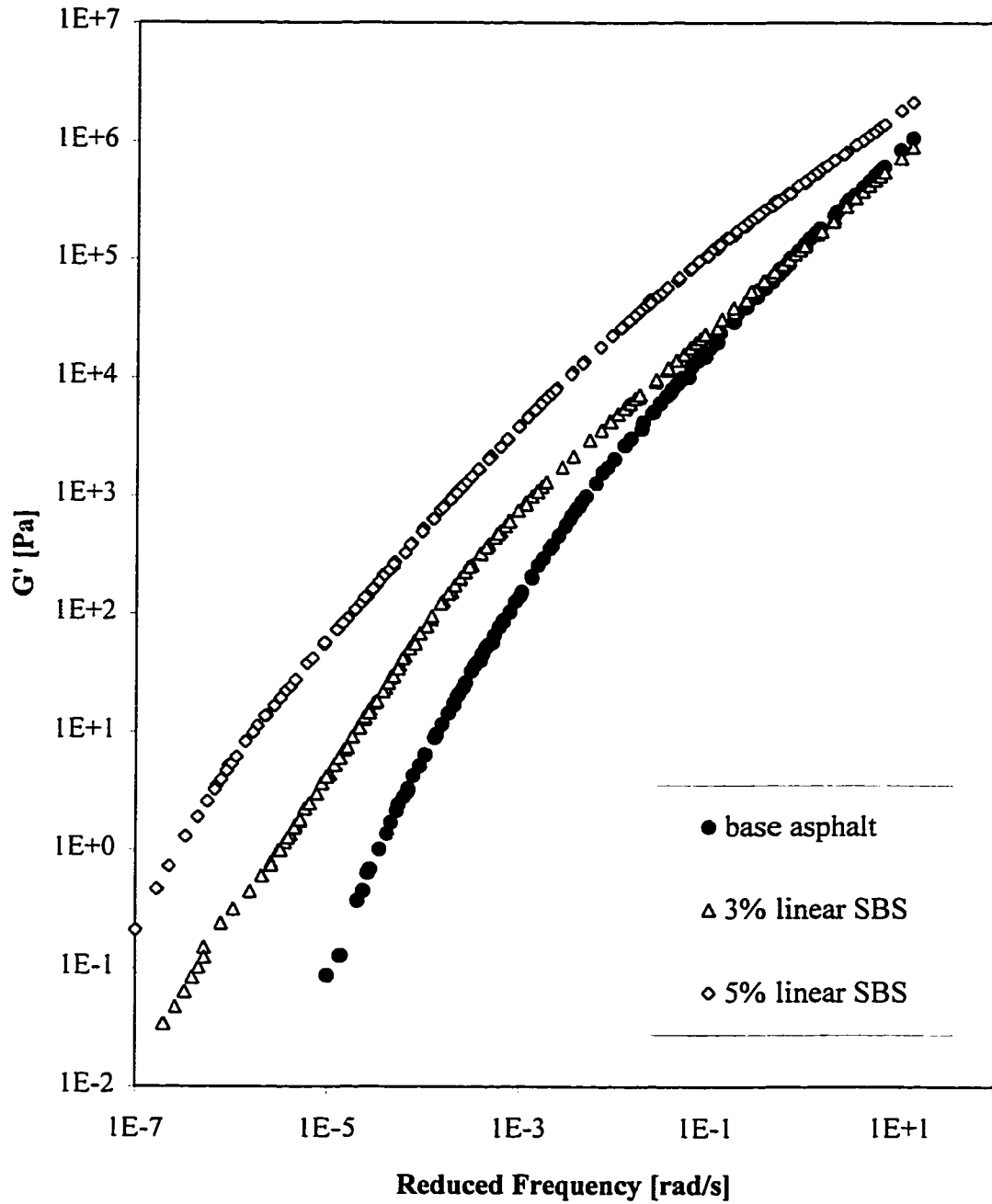


Figure 7.22 G' of Different Concentrations of Binders Modified with Linear SBS at Reference Temperature 5°C

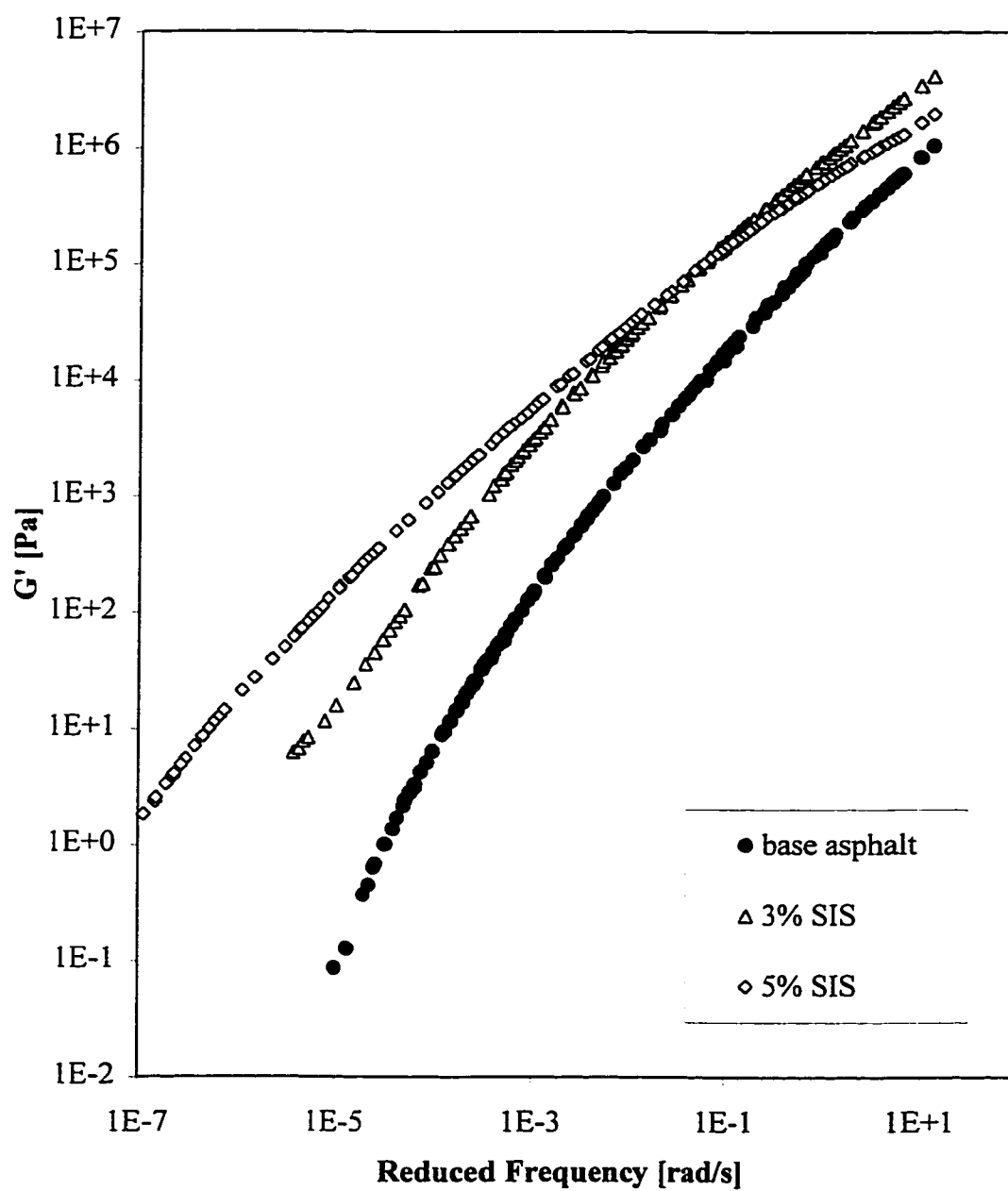


Figure 7.23 G' of Different Concentrations of Binders Modified with SIS at Reference Temperature 5 °C

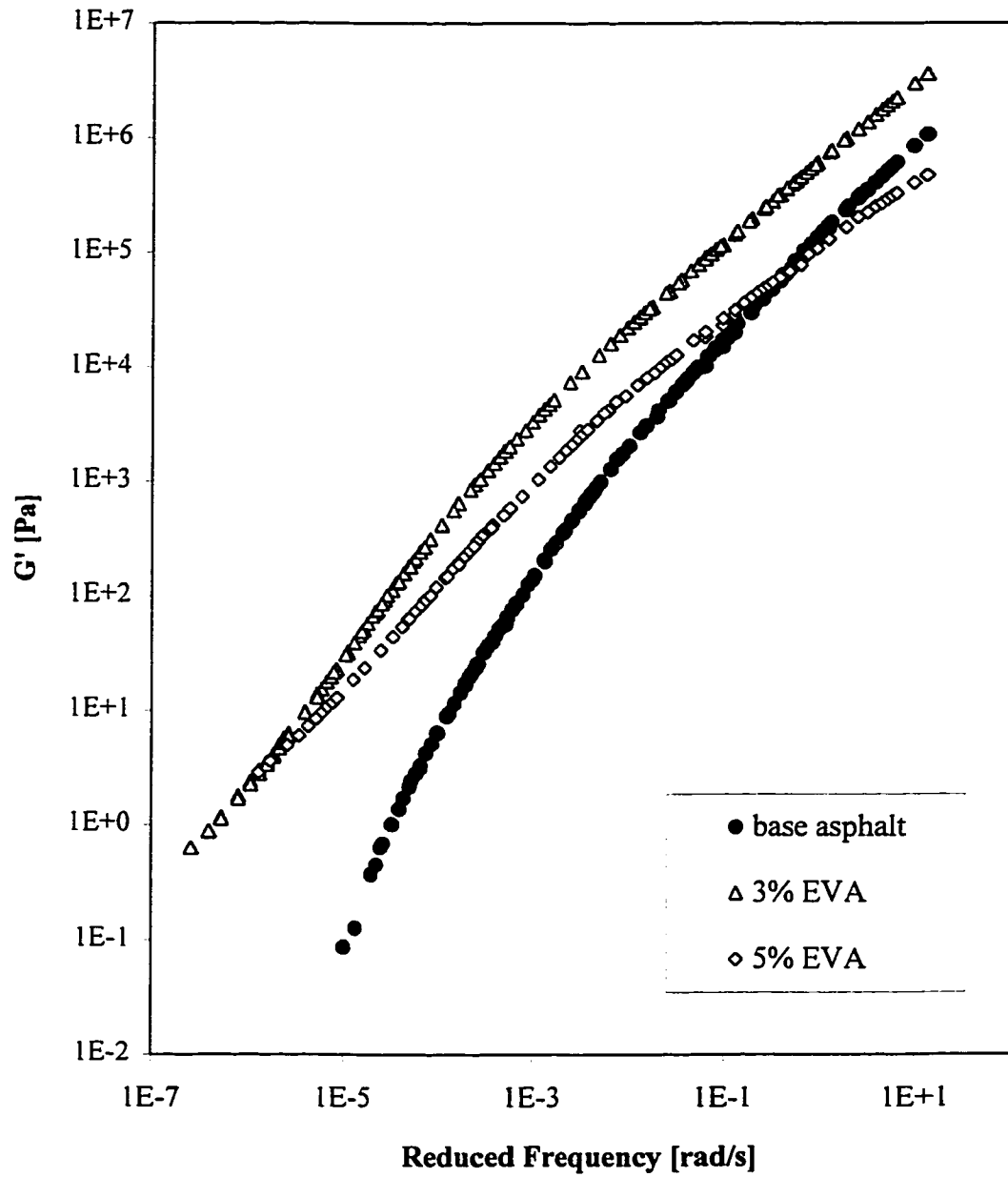


Figure 7.24 G' of Different Concentrations of Binders Modified with EVA (Elvax 350) at Reference Temperature 5 °C

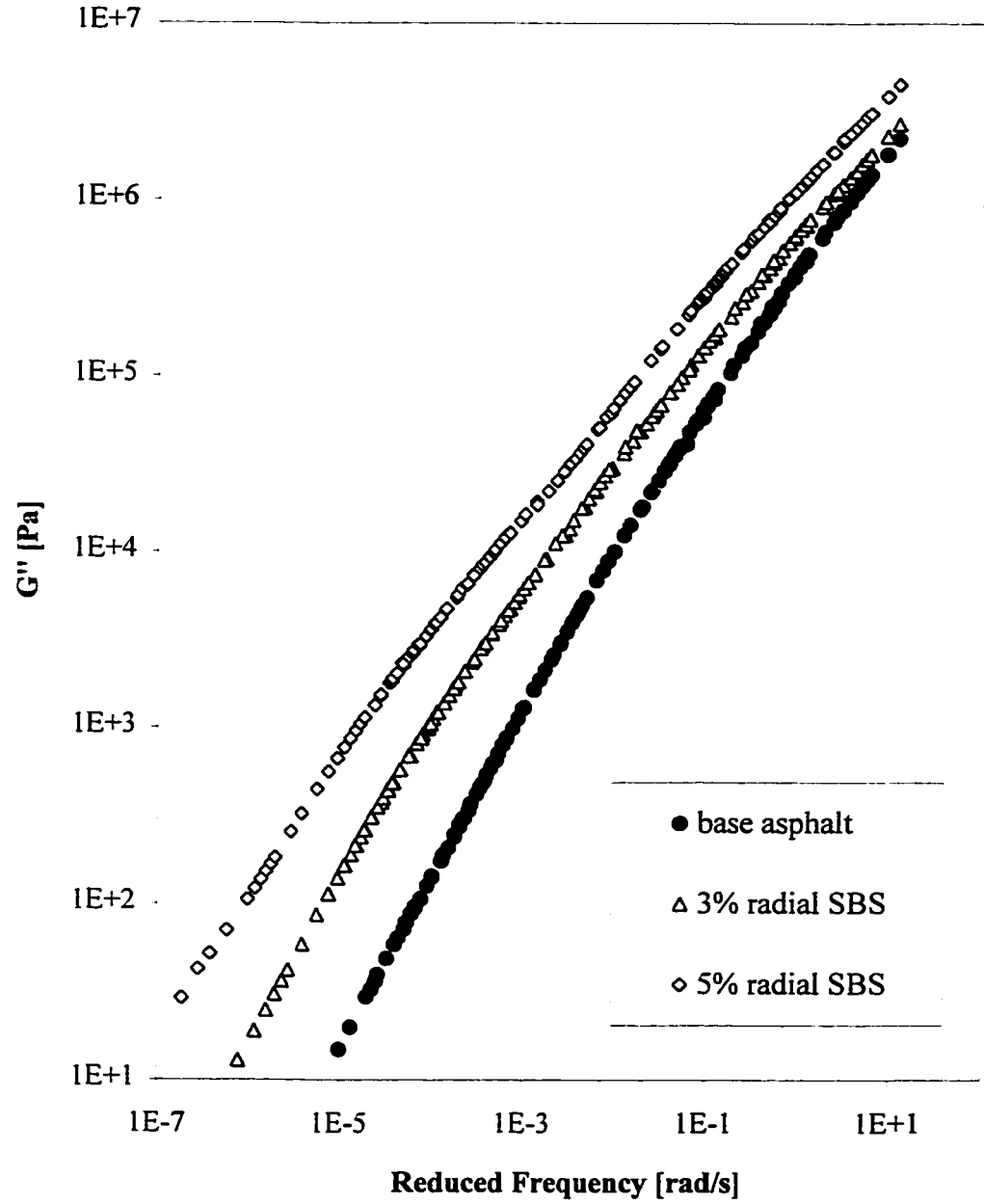


Figure 7.25 G'' of Different Concentrations of Binders Modified with Radial SBS at Reference Temperature 5 °C

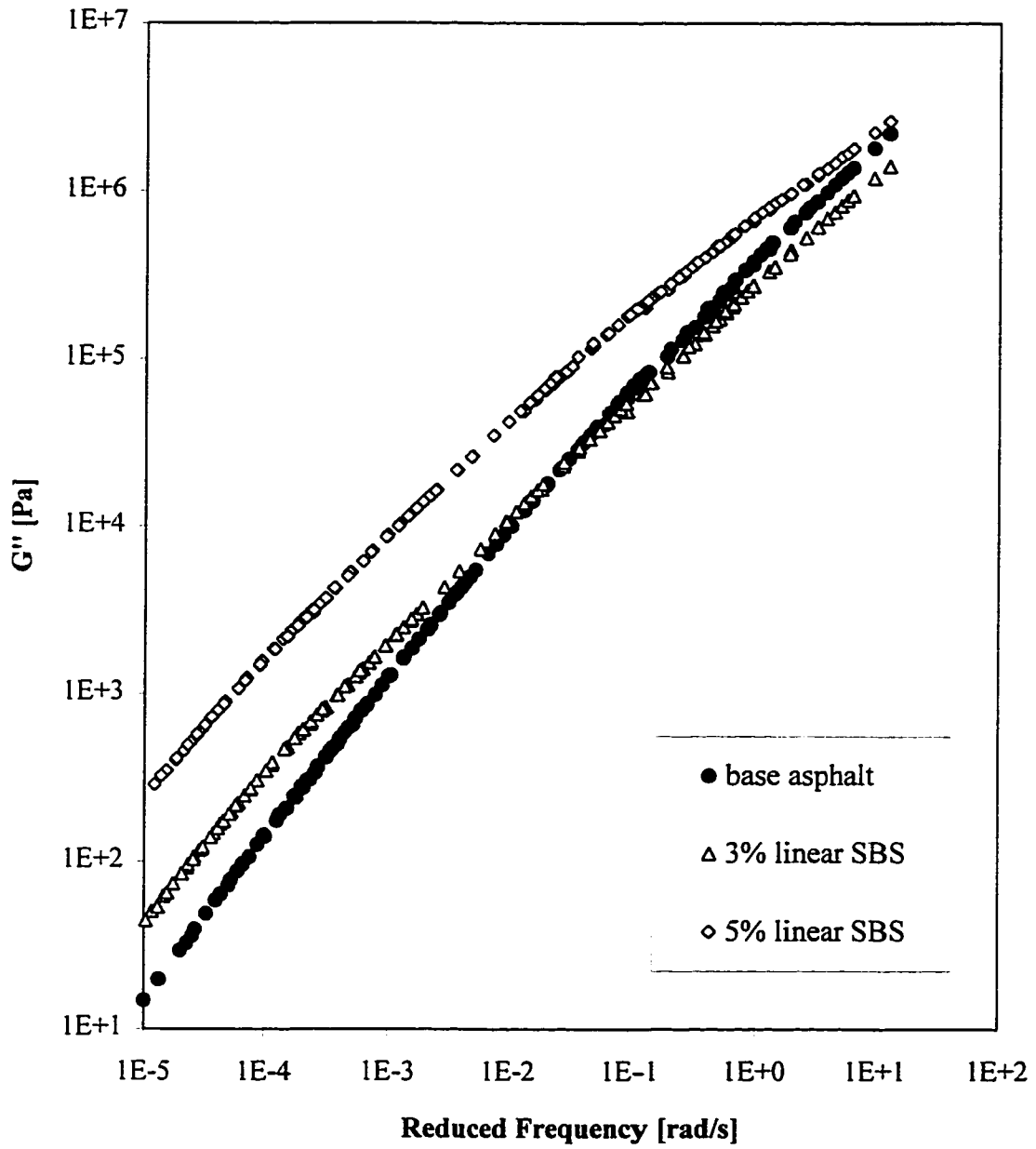


Figure 7.26 G'' of Different Concentrations of Binders Modified with Linear SBS at Reference Temperature 5°C

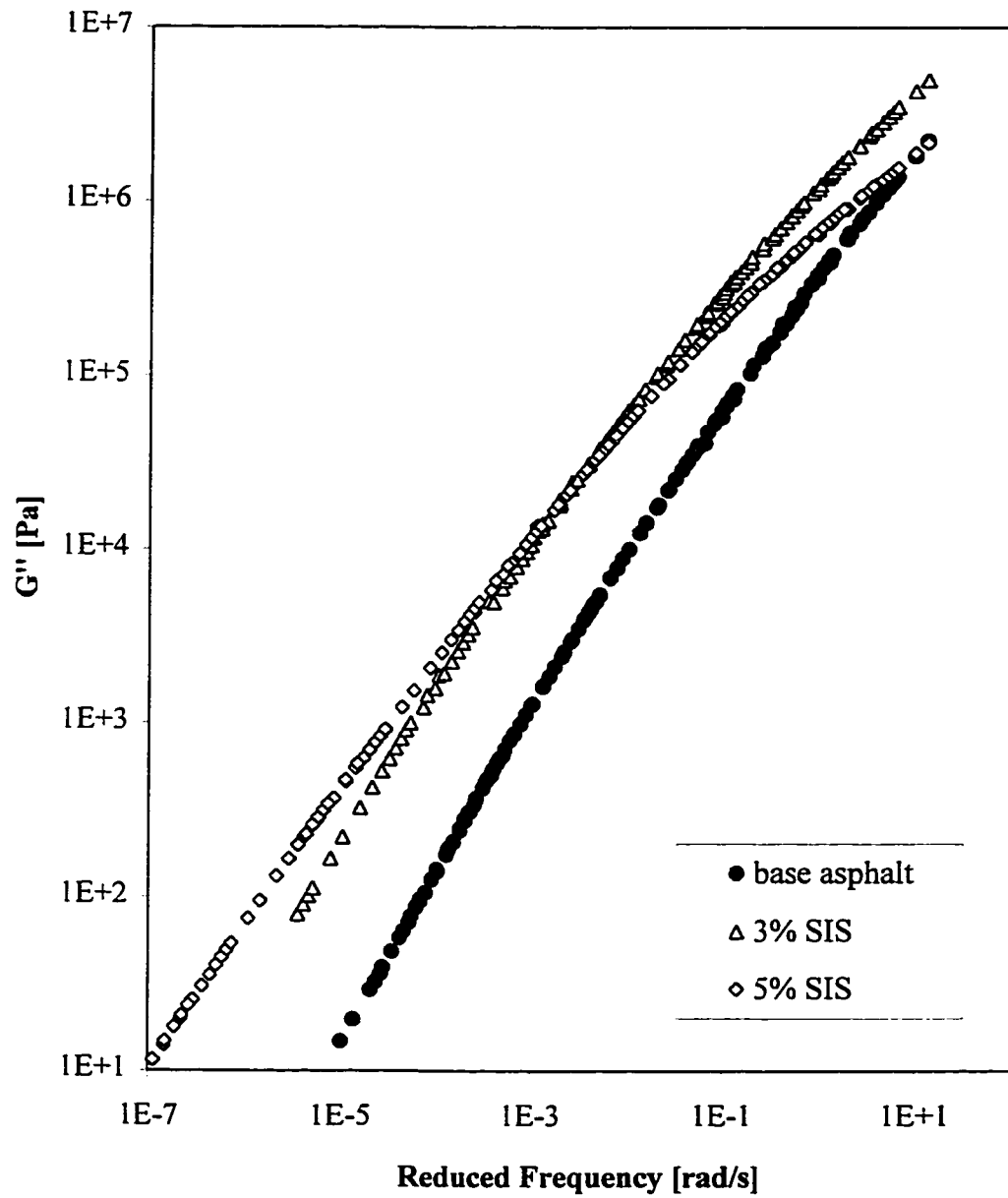


Figure 7.27 G'' of Different Concentrations of Binders Modified with SIS at Reference Temperature 5°C

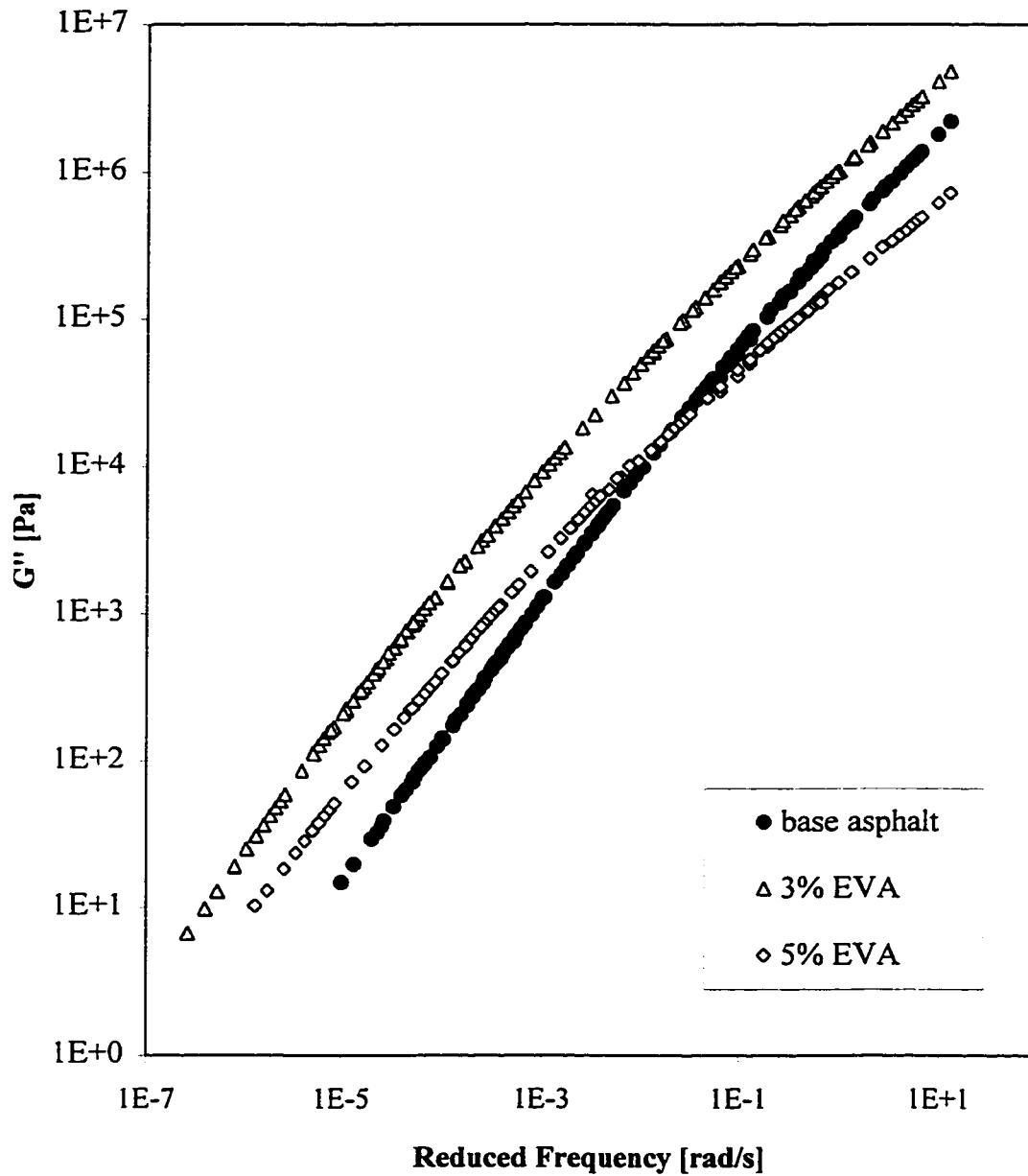


Figure 7.28 G'' of Different Concentrations of Binders Modified with EVA (Elvax 350) at Reference Temperature 5°C

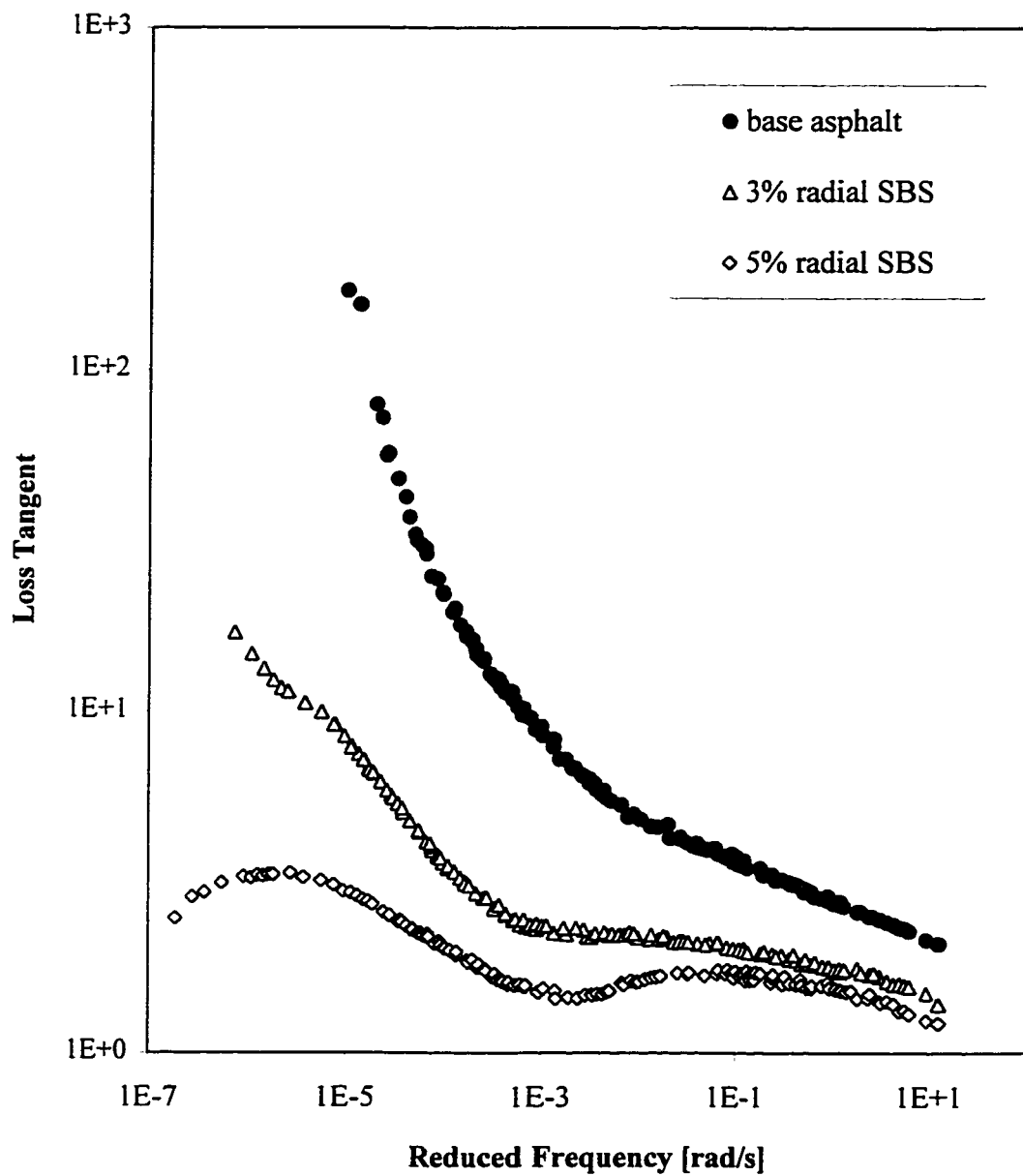


Figure 7.29 Loss Tangents of Different Concentrations of Binders Modified with Radial SBS at Reference Temperature 5 °C

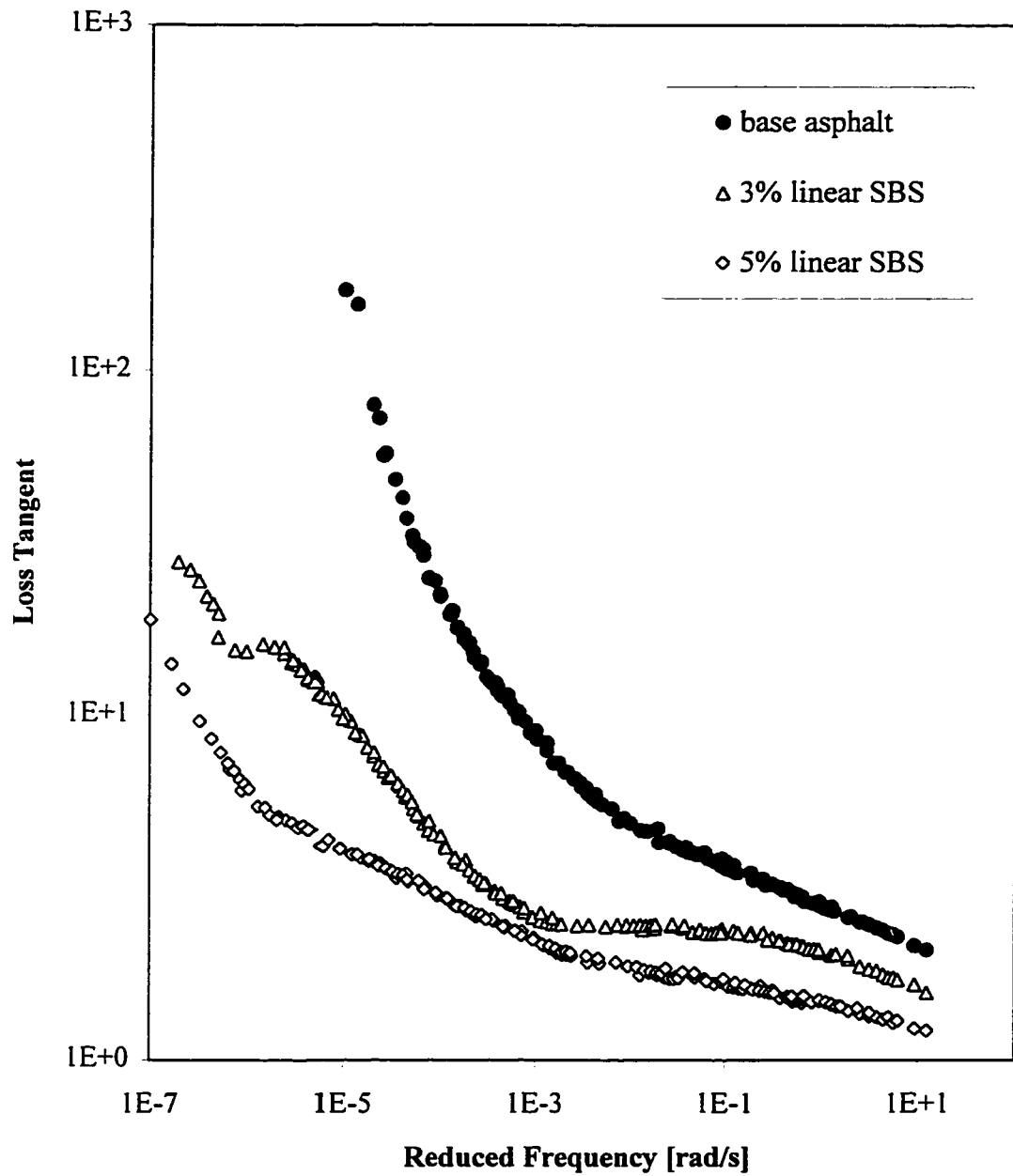


Figure 7.30 Loss Tangents of Different Concentrations of Binders Modified with Linear SBS at Reference Temperature 5 °C

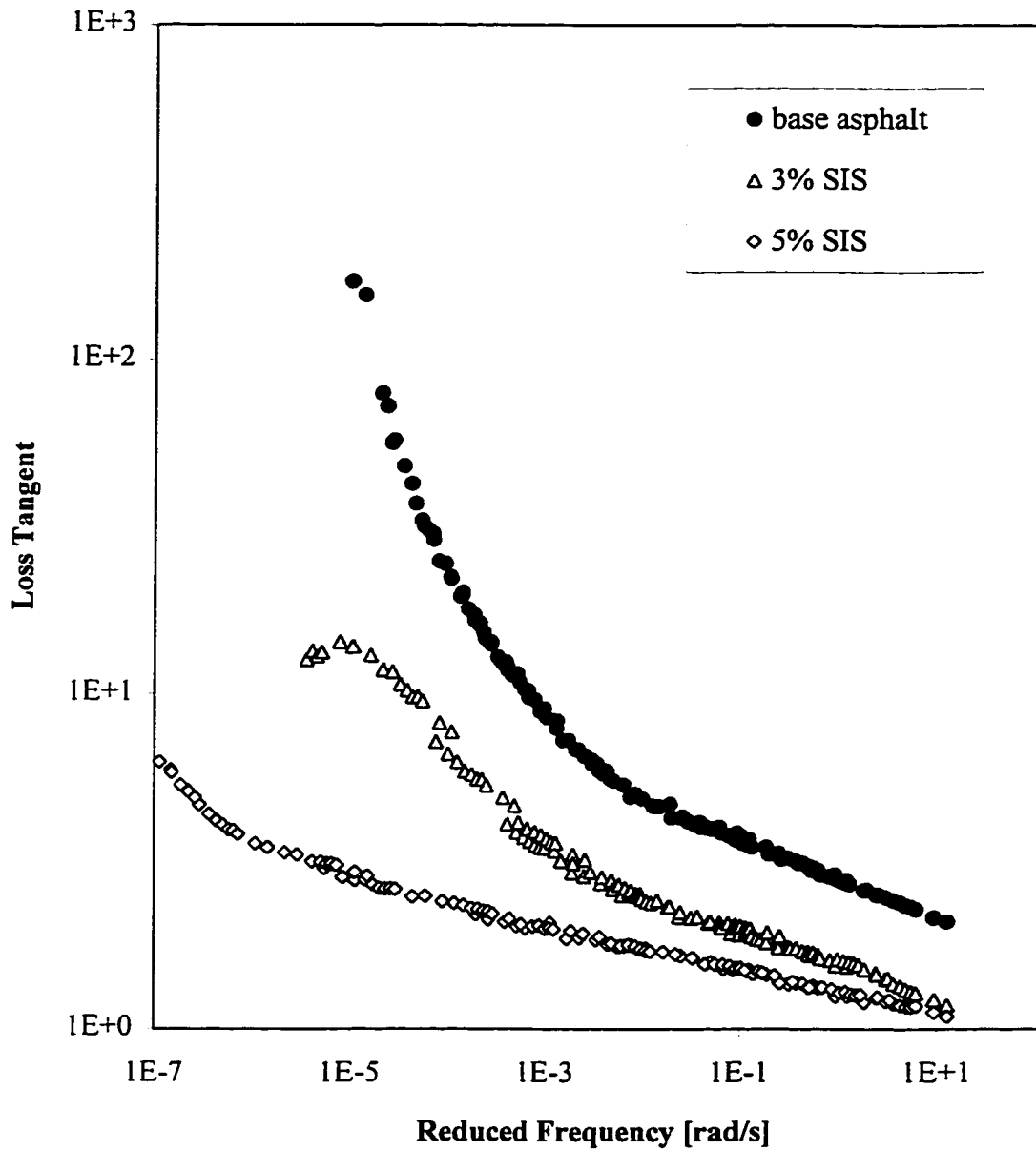


Figure 7.31 Loss Tangents of Different Concentrations of Binders Modified with SIS at Reference Temperature 5 °C

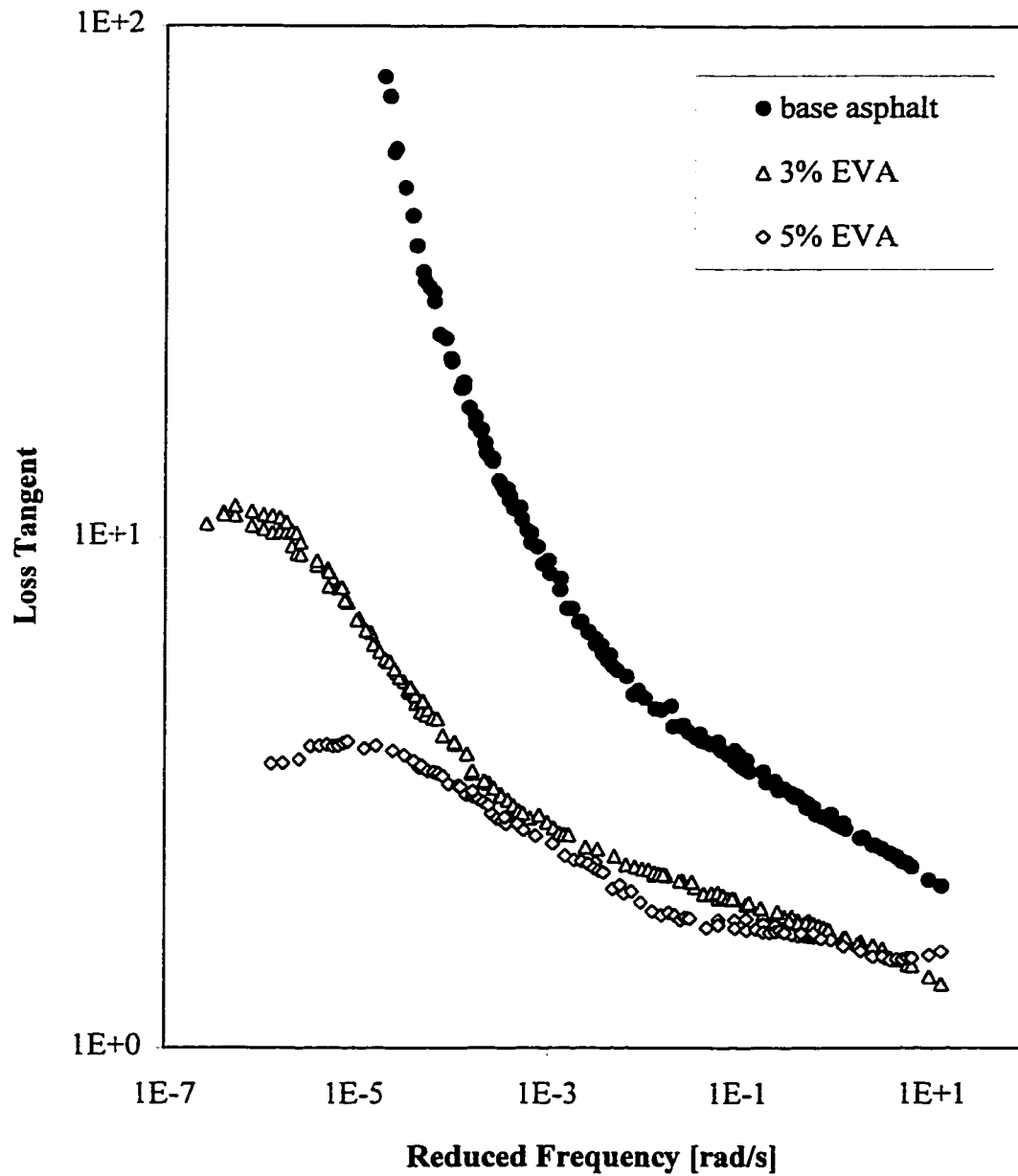


Figure 7.32 Loss Tangent of Different Concentrations of Binders Modified with EVA (Elvax 350) at Reference Temperature 5 °C

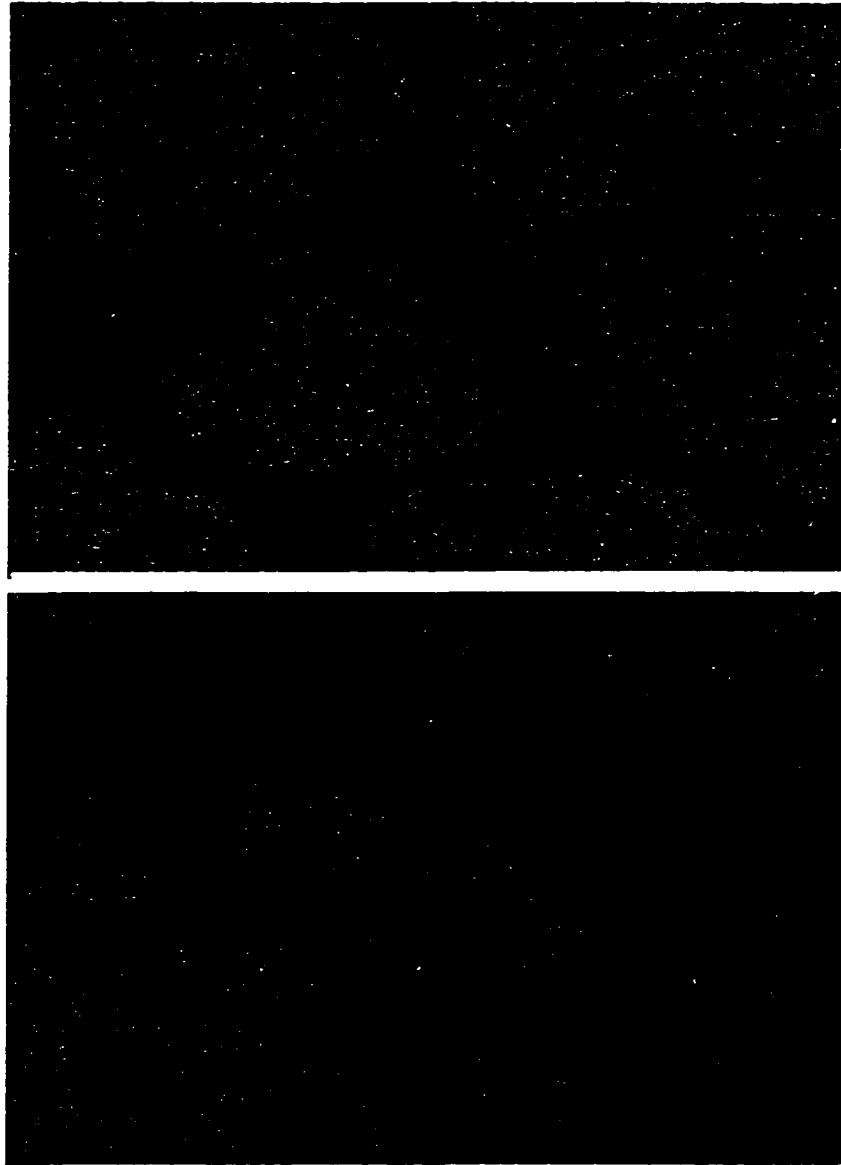


Figure 7.33 Micrographs of Binders Modified with 3% Radial SBS (Finaprene 411)
Enlargements are 40x (Top) and 10x (Bottom)

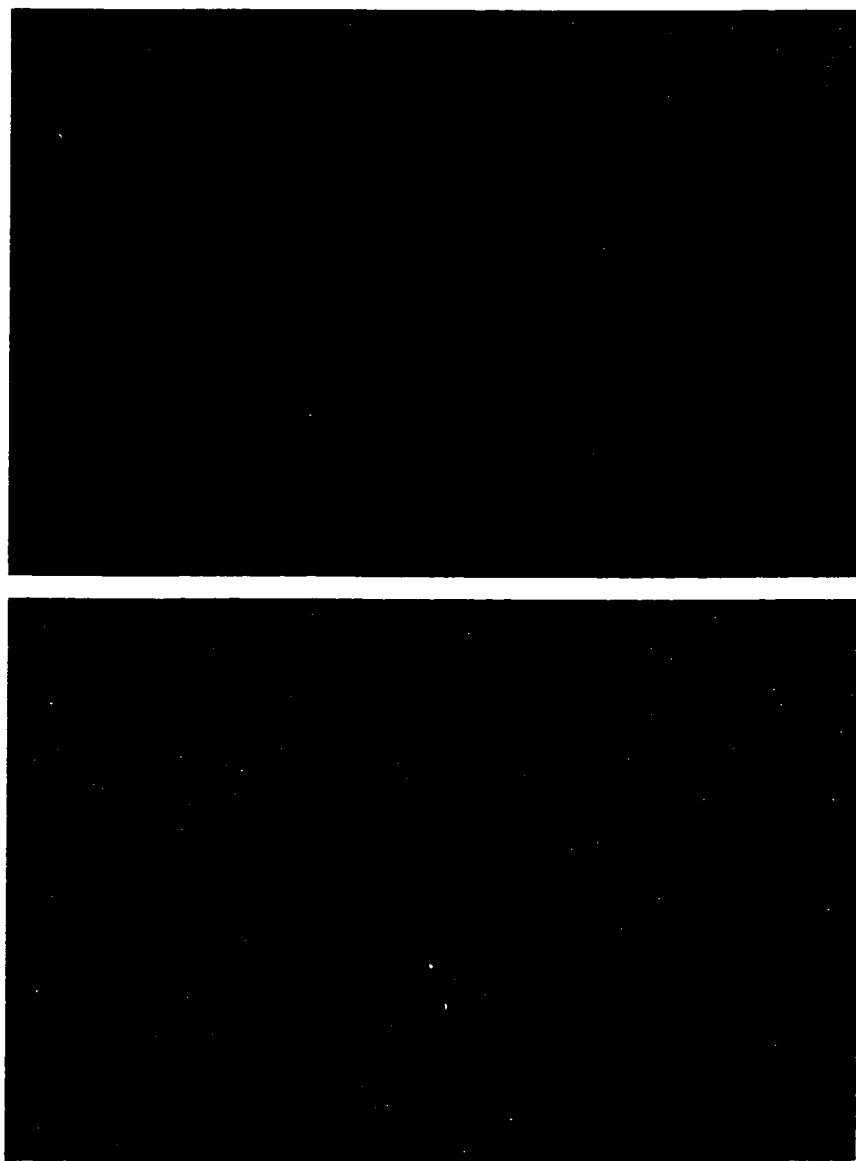


Figure 7.34 Micrographs of Binders Modified with 5% Radial SBS (Finaprene 411)
Enlargements are 40x (Top) and 10x (Bottom)

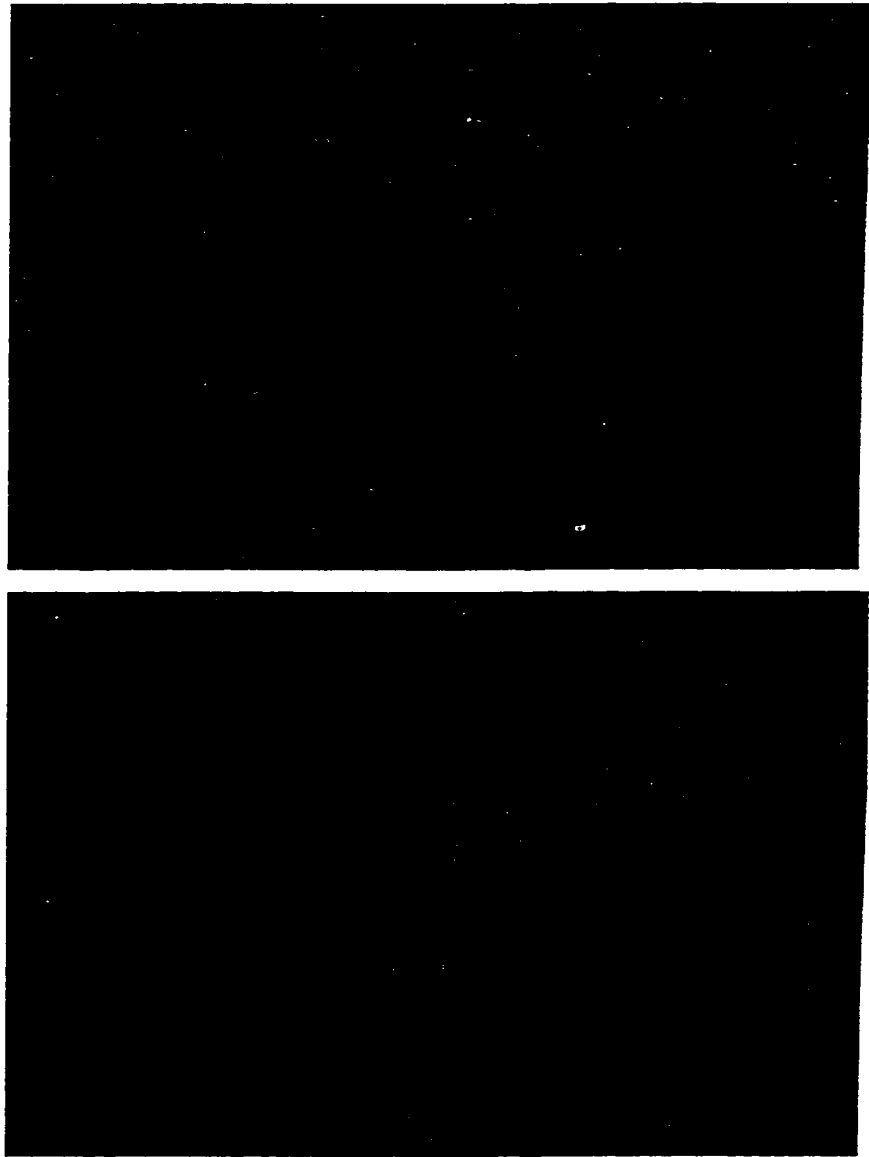


Figure 7.35 Micrographs of Binders Modified with 7% Radial SBS (Finaprene 411)
Enlargements are 40x (Top) and 10x (Bottom)

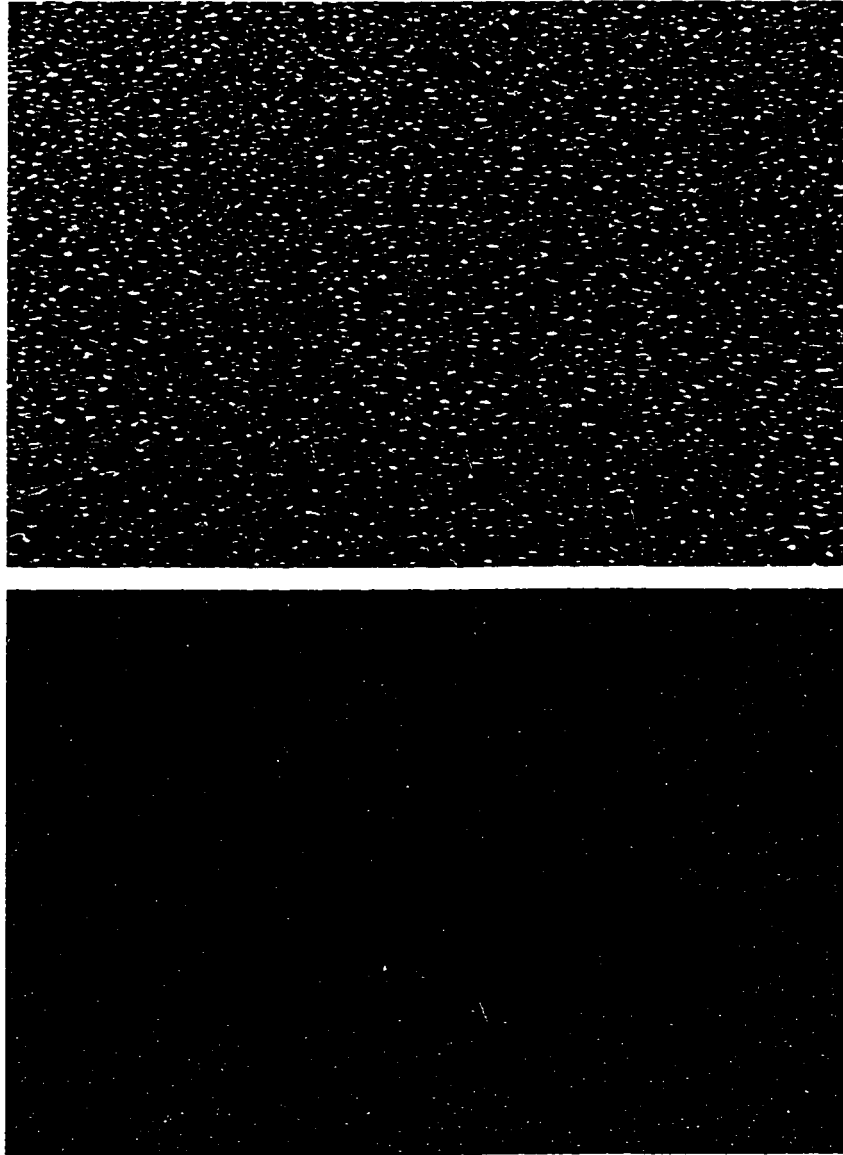


Figure 7.36 Micrographs of Binders Modified with 3% Linear SBS (Kraton D1102)
Enlargements are 40x (Top) and 10x (Bottom)

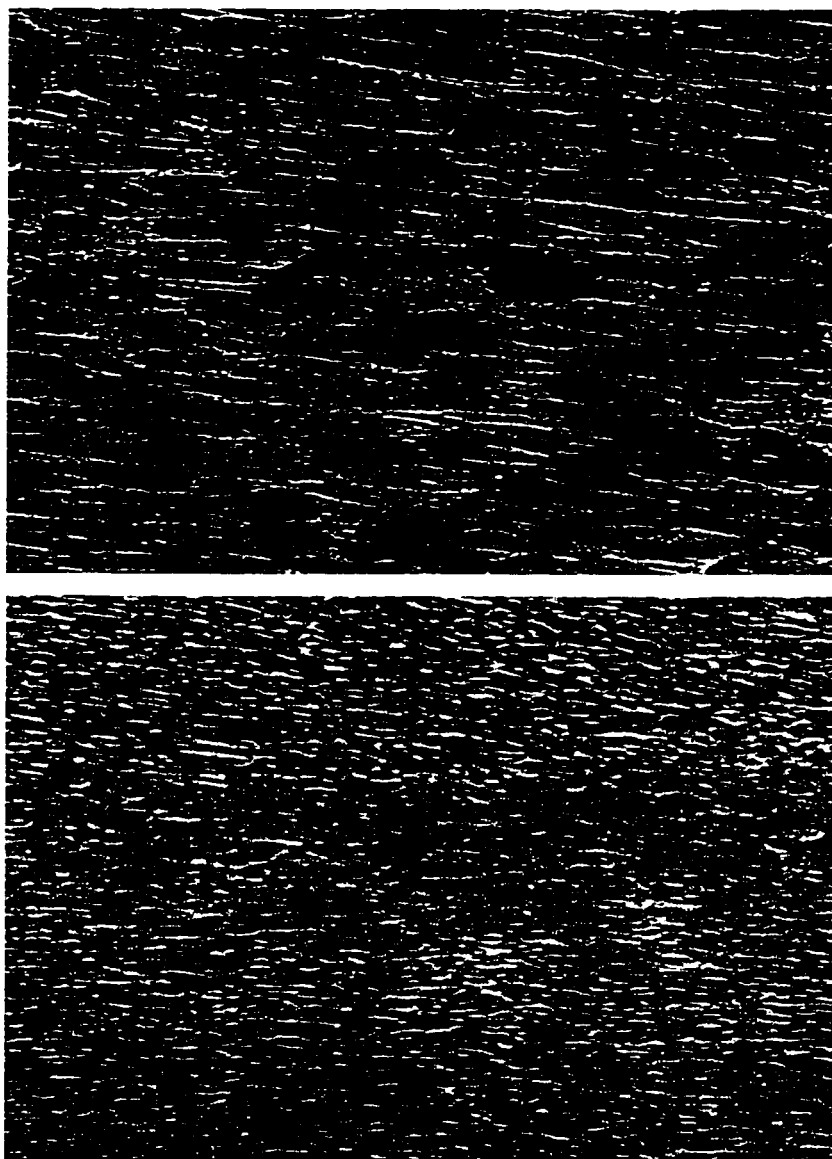


Figure 7.37 Micrographs of Binders Modified with 5% Linear SBS (Kraton D1102)
Enlargements are 40x (Top) and 10x (Bottom)

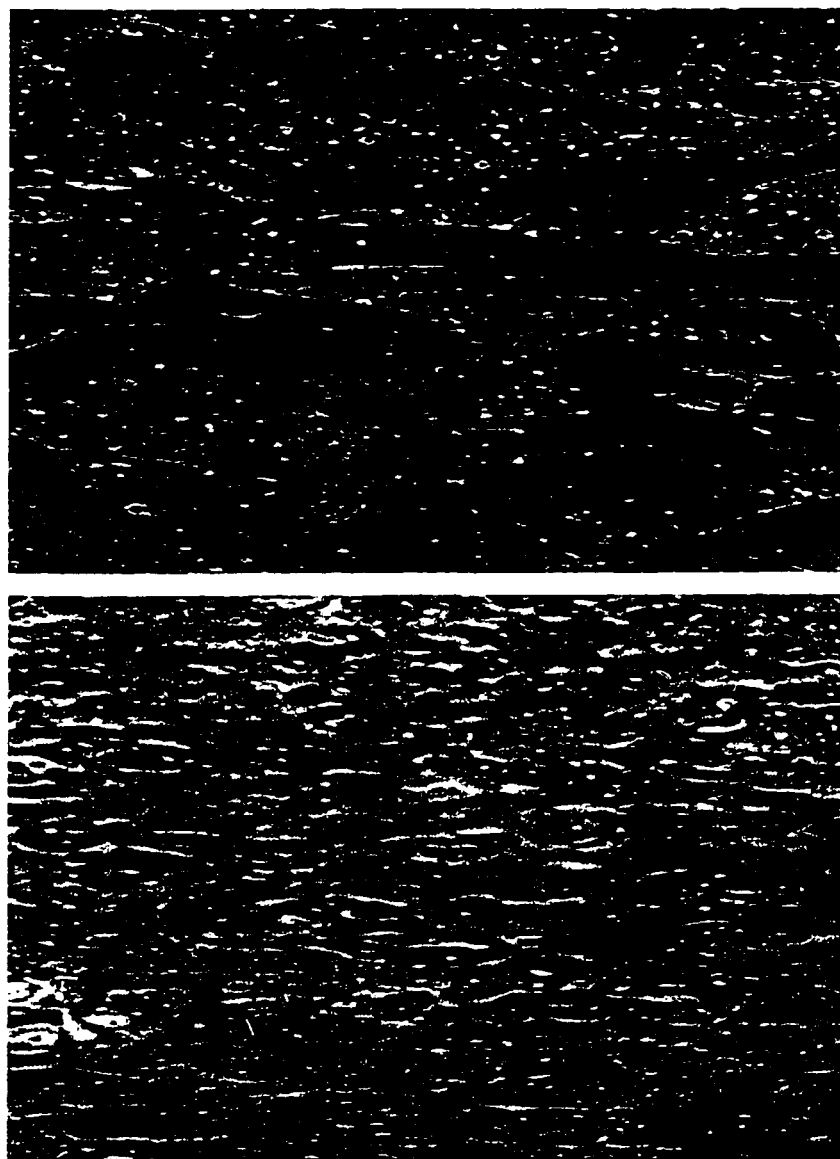


Figure 7.38 Micrographs of Binders Modified with 7% Linear SBS (Kraton D1102)
Enlargements are 40x (Top) and 10x (Bottom)

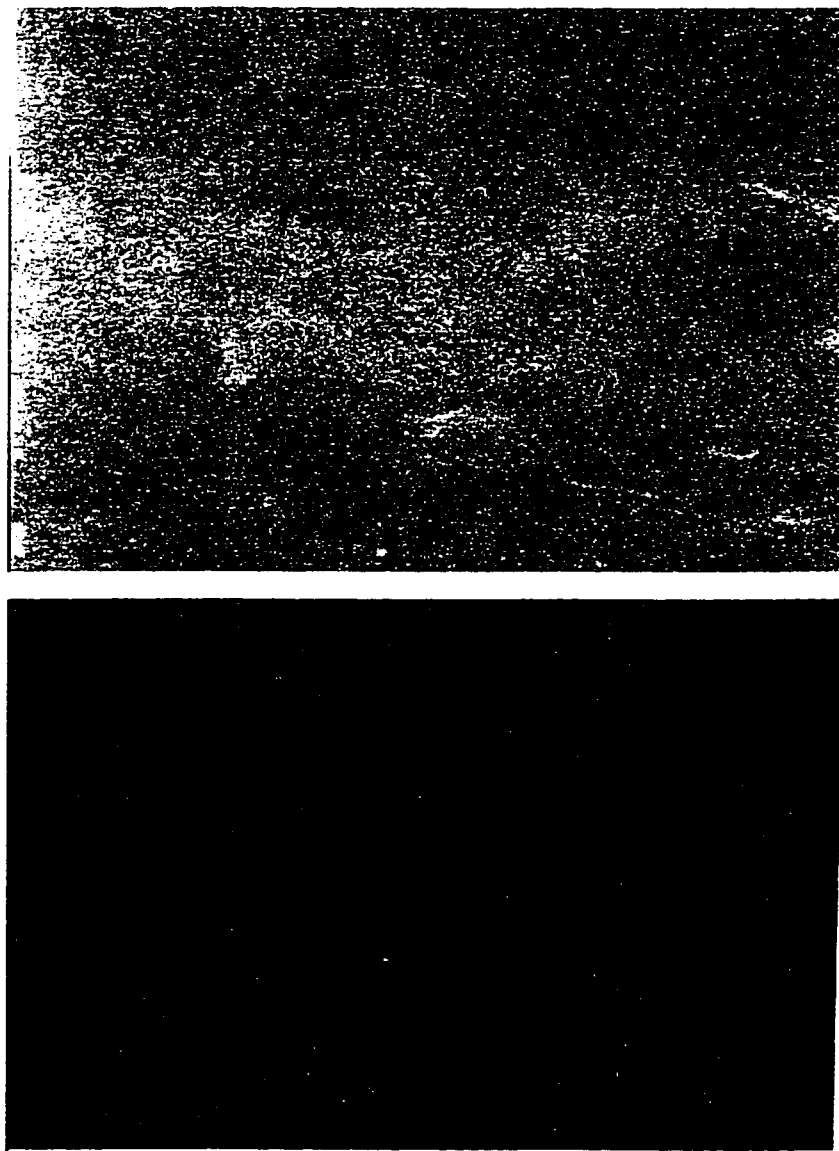


Figure 7.39 Micrographs of Binder Modified with 3% SIS (Kraton D1107) (Top) and Base Asphalt (Bottom)

Enlargements are 40x (Top and Bottom)

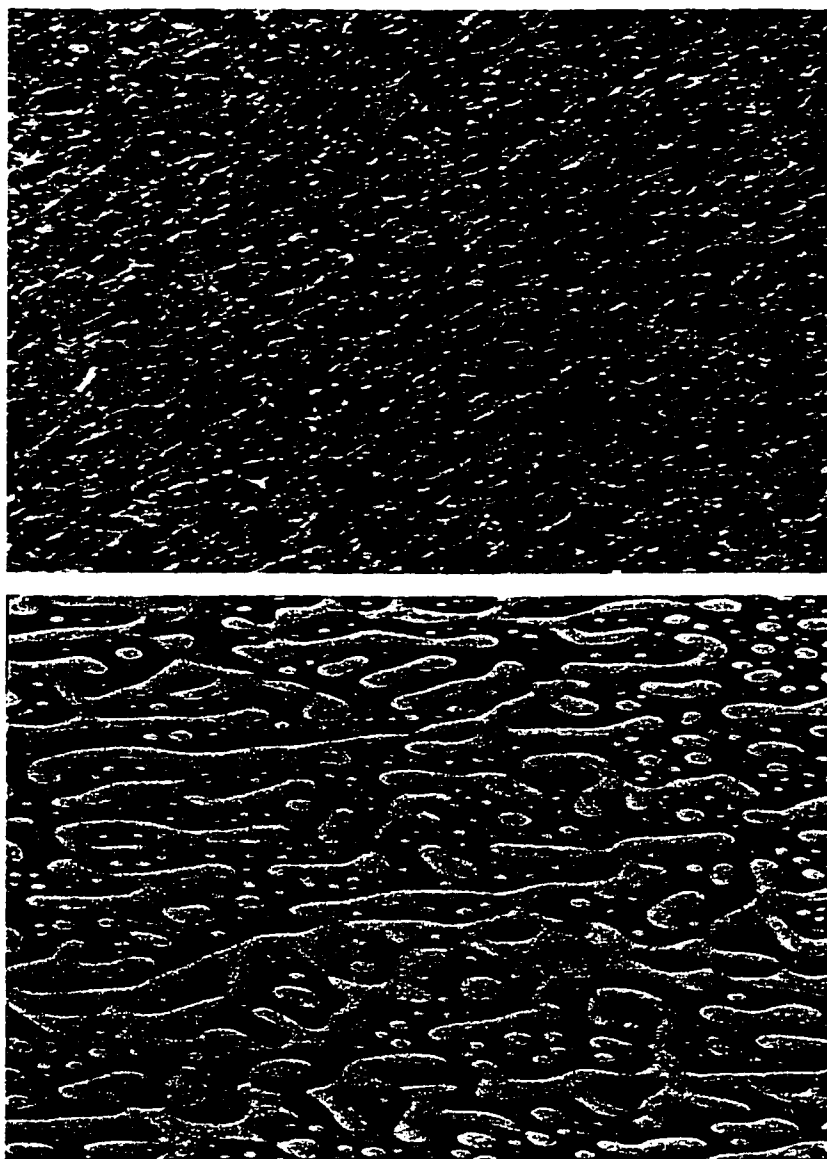


Figure 7.40 Micrographs of Binders Modified with 5% SIS (Kraton D1107)
Enlargements are 40x (Top) and 10x (Bottom)

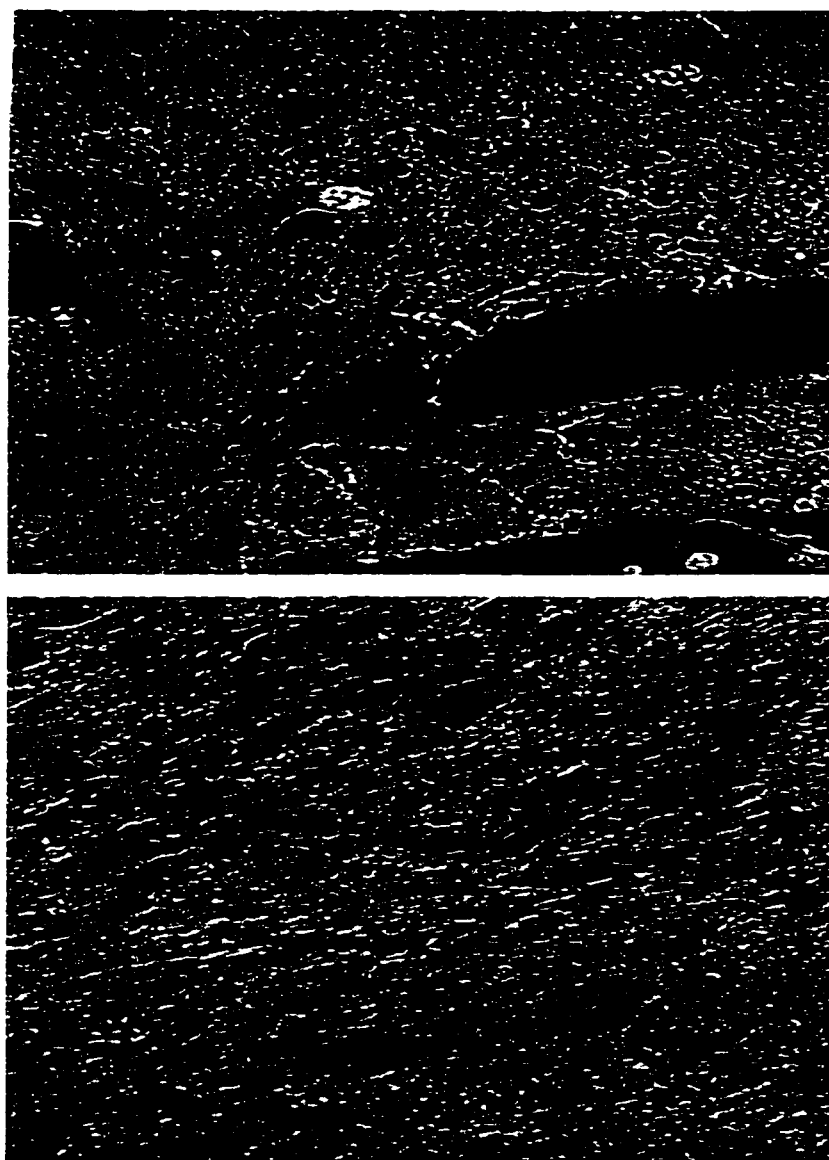


Figure 7.41 Micrographs of Binders Modified with 7% SIS (Kraton D1107)
Enlargements are 40x (Top) and 10x (Bottom)

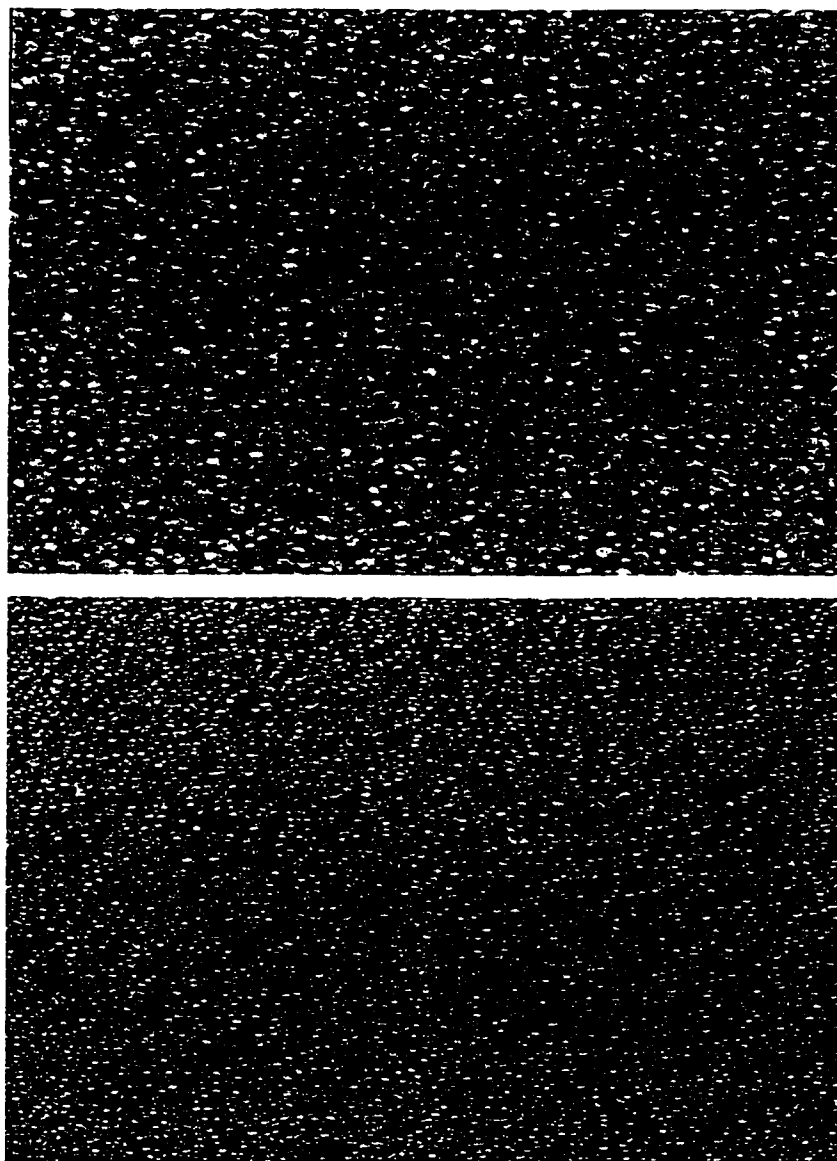


Figure 7.42 Micrographs of Binders Modified with 3% EVA (Elvax 150W)
Enlargements are 40x (Top) and 10x (Bottom)

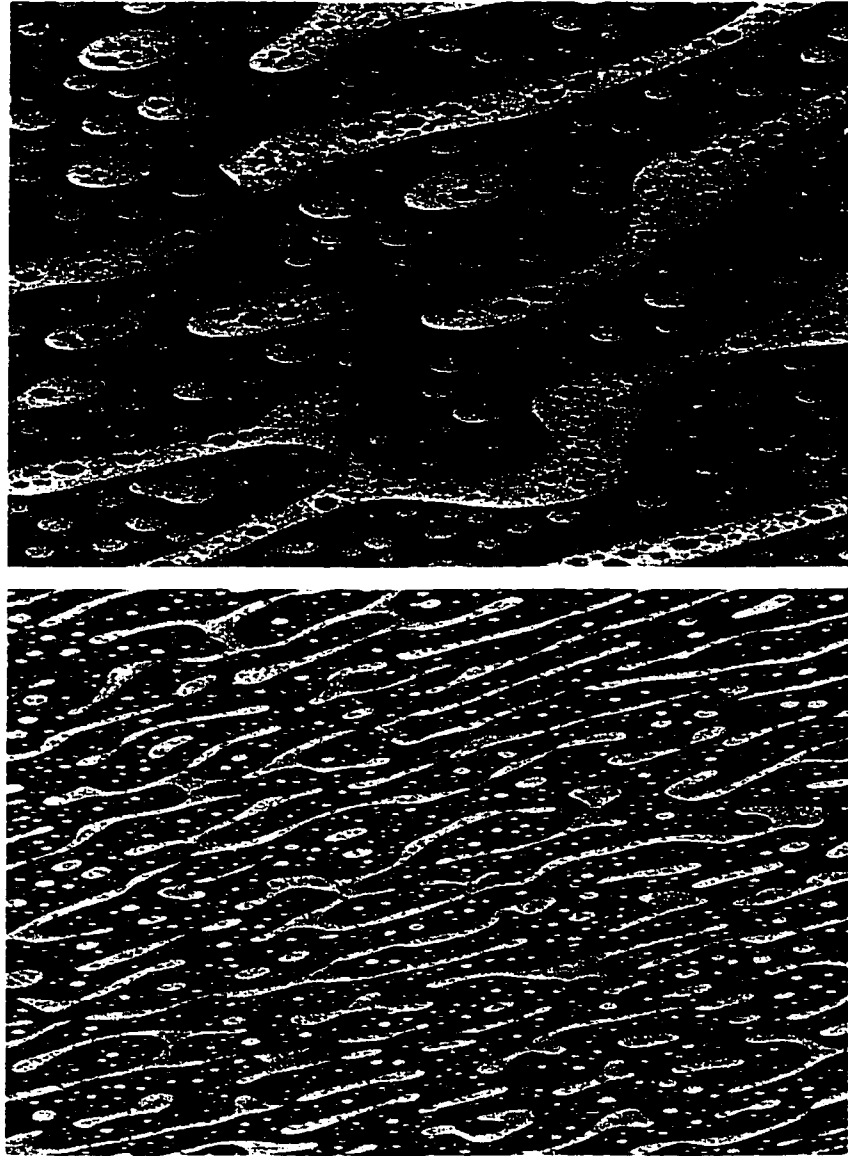


Figure 7.43 Micrographs of Binders Modified with 5% EVA (Elvax 150W)
Enlargements are 40x (Top) and 10x (Bottom)

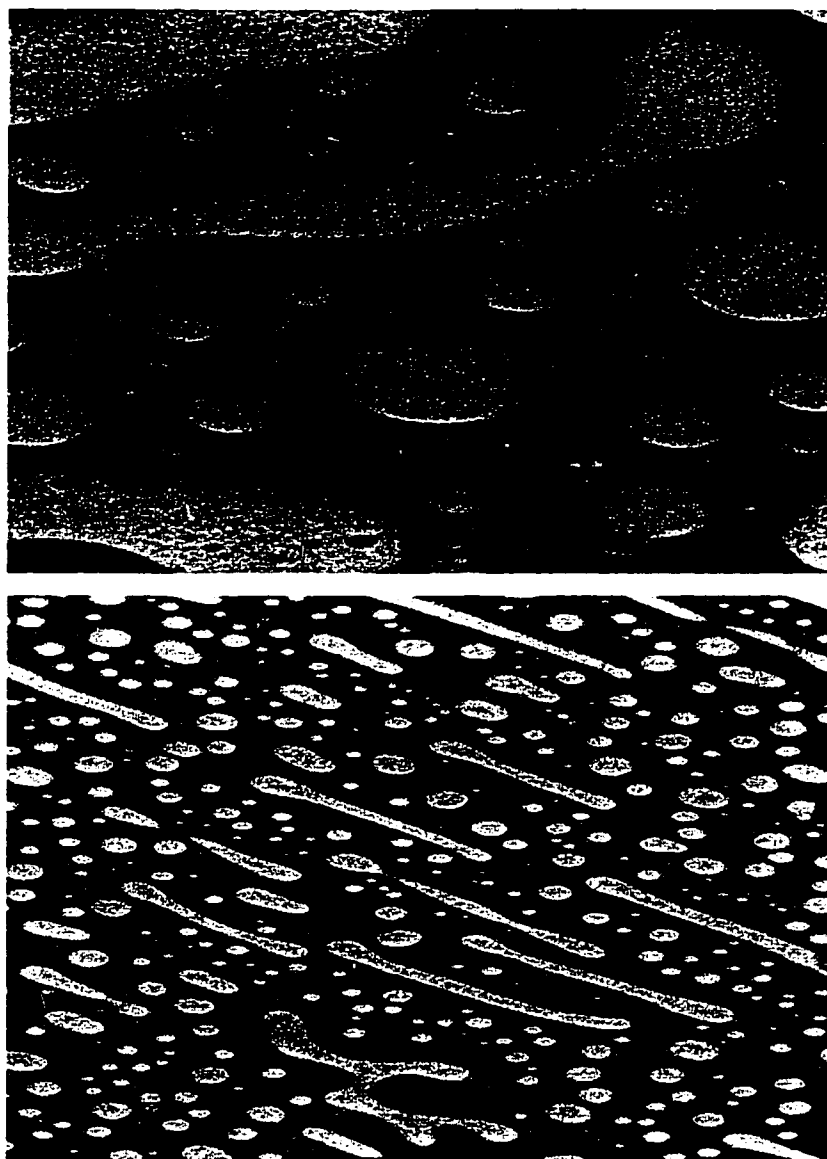


Figure 7.44 Micrographs of Binders Modified with 7% EVA (Elvax 150W)
Enlargements are 40x (Top) and 10x (Bottom)

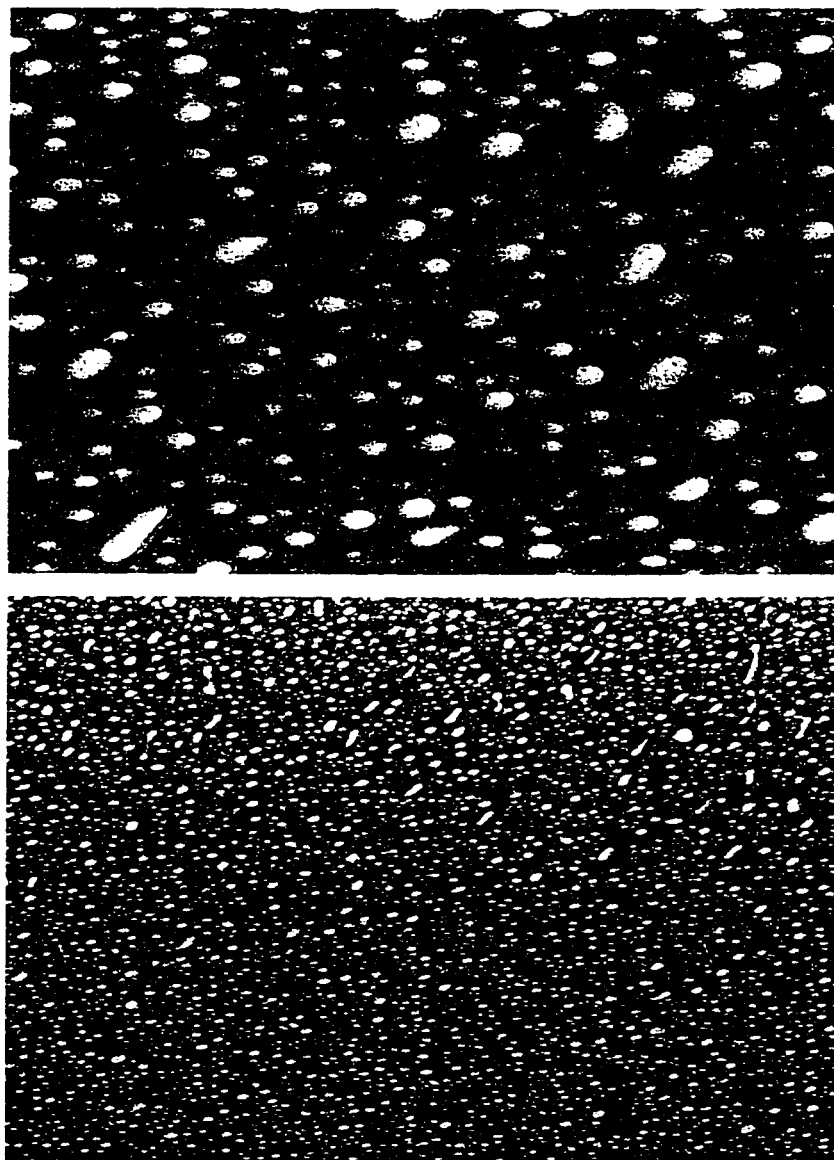


Figure 7.45 Micrographs of Binders Modified with 3% EVA (Elvax 350)
Enlargements are 40x (Top) and 10x (Bottom)

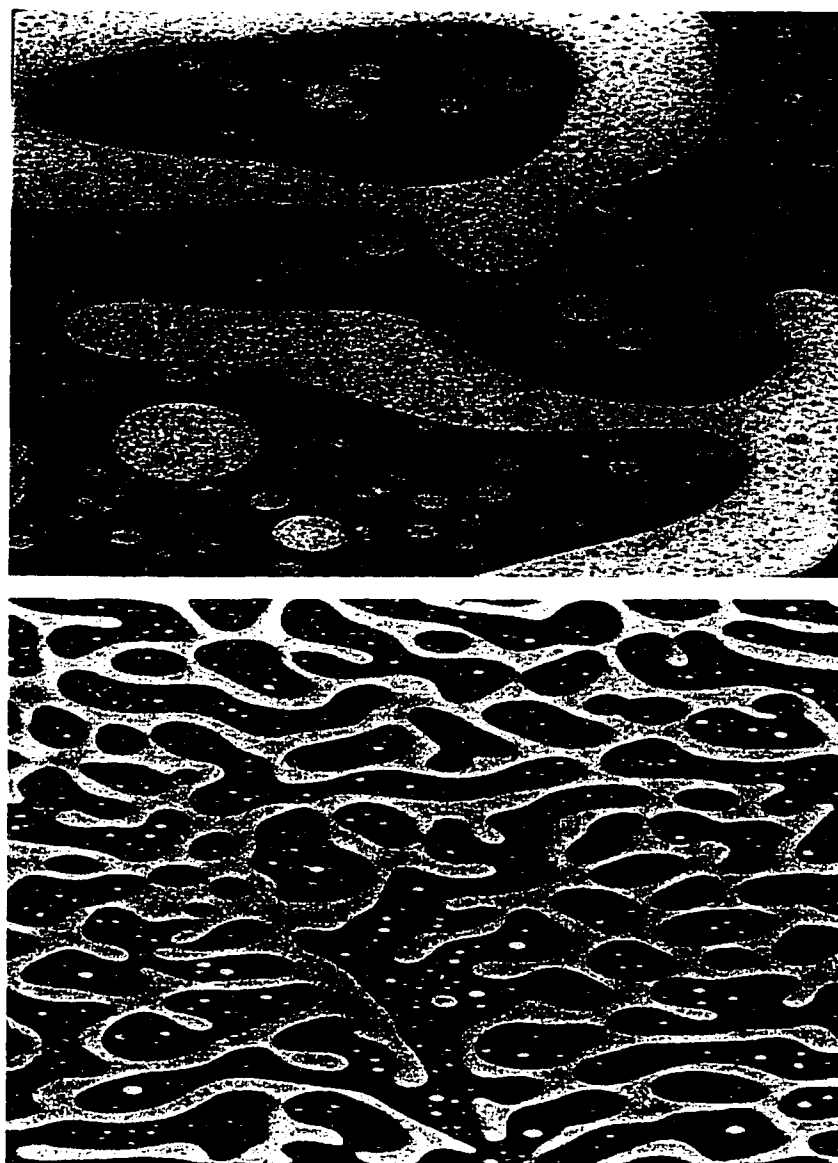


Figure 7.46 Micrographs of Binders Modified with 5% EVA (Elvax 350)
Enlargements are 40x (Top) and 10x (Bottom)

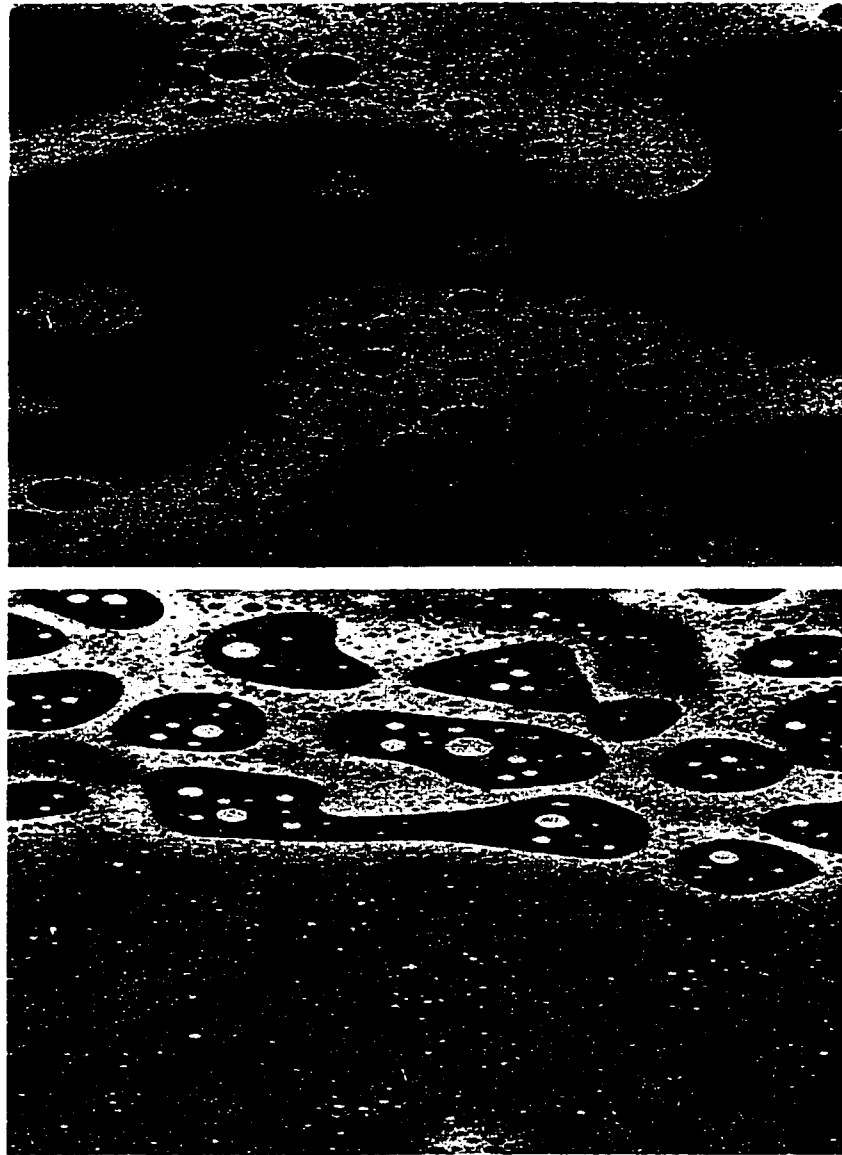


Figure 7.47 Micrographs of Binders Modified with 7% EVA (Elvax 350)
Enlargements are 40x (Top) and 10x (Bottom)

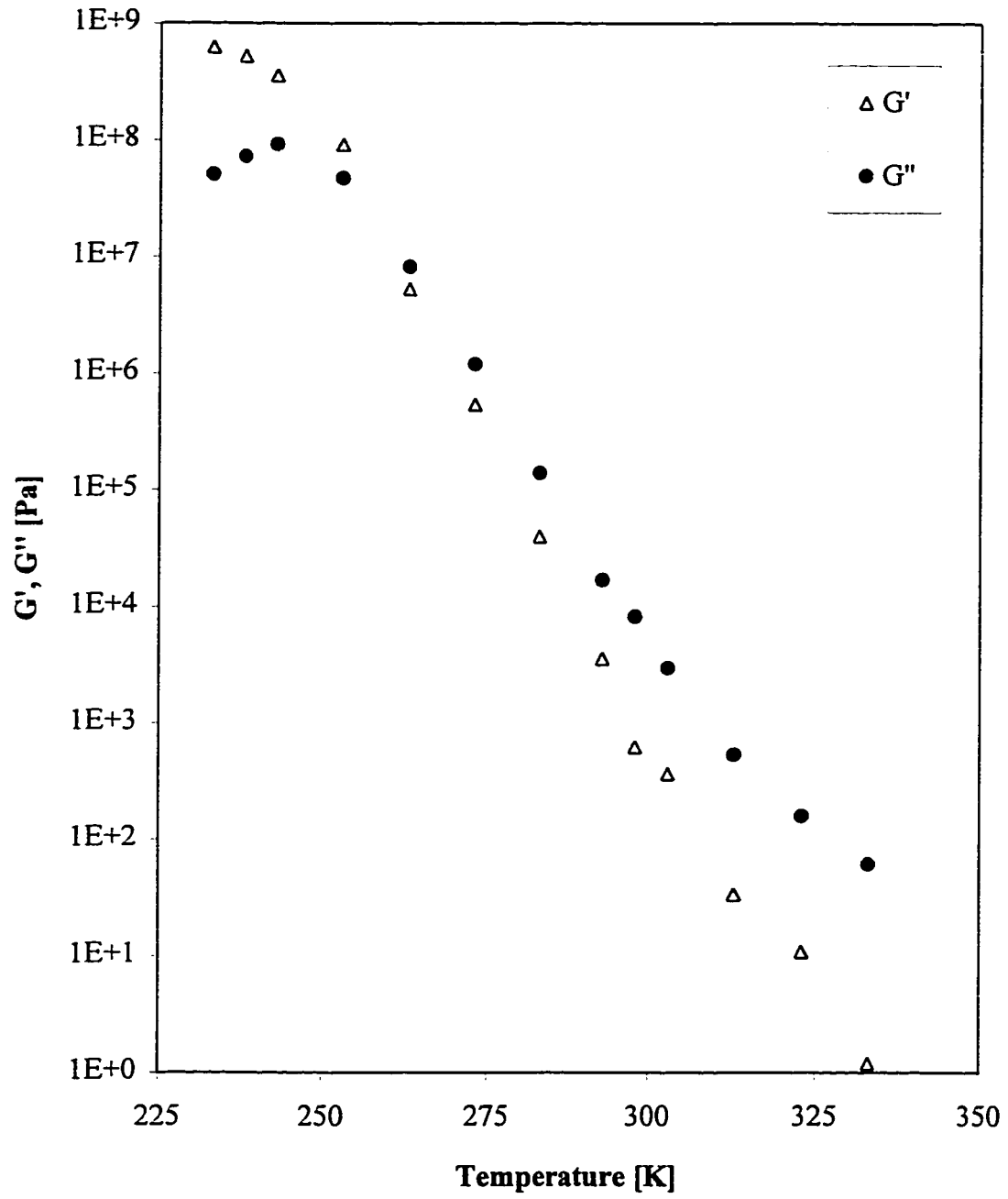


Figure 7.48 G' and G'' of Base Asphalt at Frequency 0.1 Hz

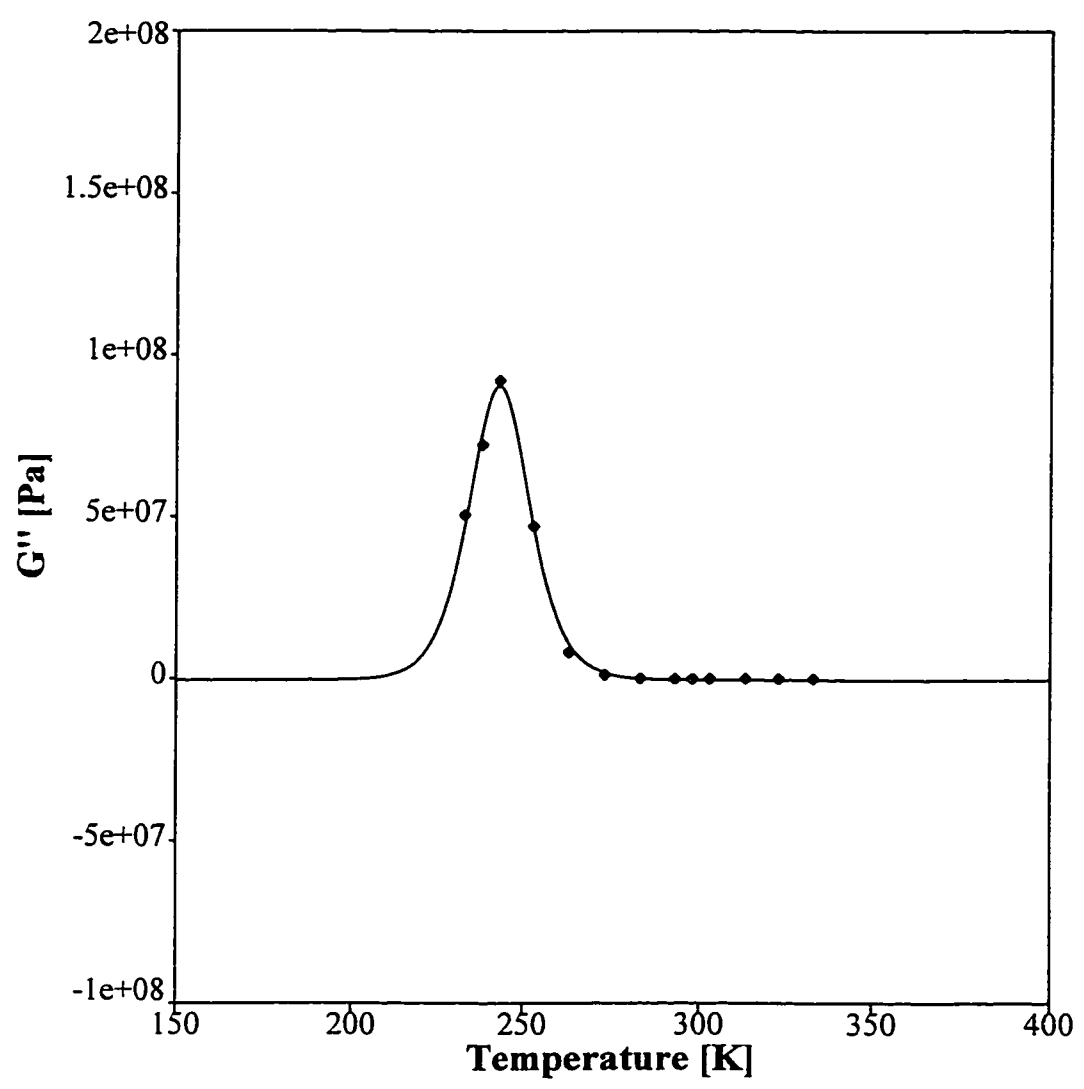


Figure 7.49 Peak Function of Base Asphalt at Frequency 0.1 Hz

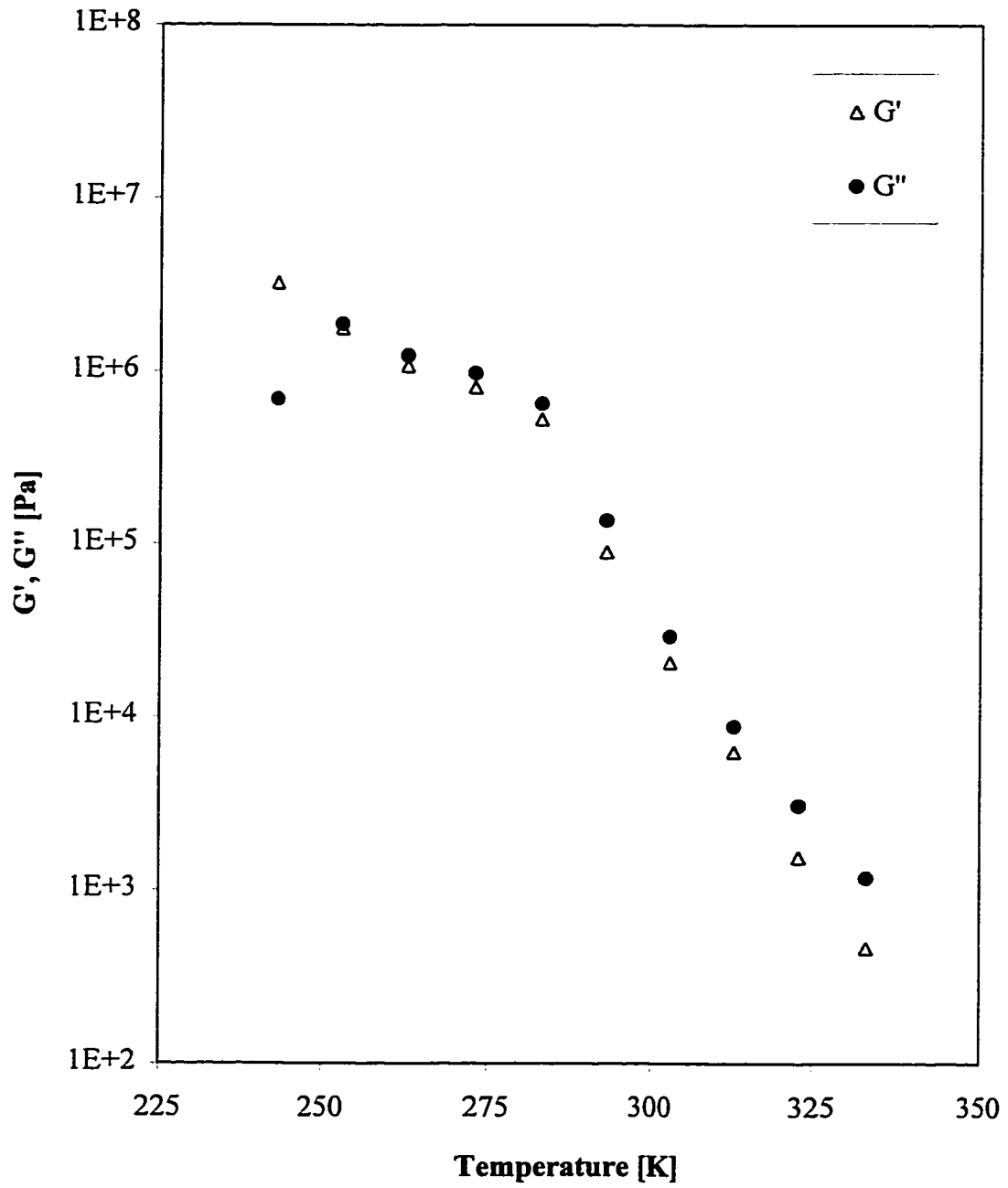


Figure 7.50 G' and G'' of Binder Modified with 5% Radial SBS at Frequency 0.1 Hz

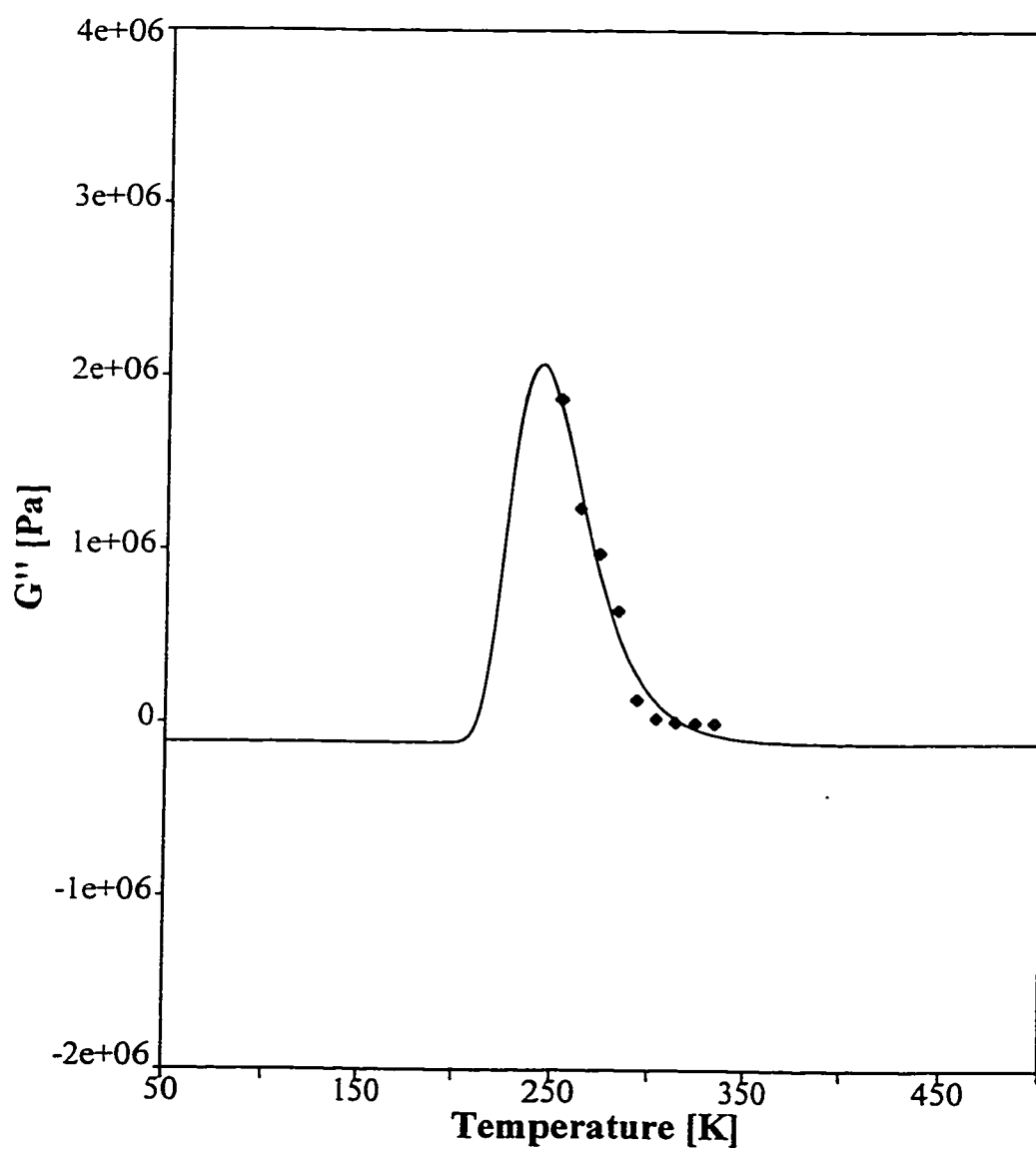


Figure 7.51 Peak Function of Binder Modified with 5% Radial SBS at Frequency 0.1 Hz

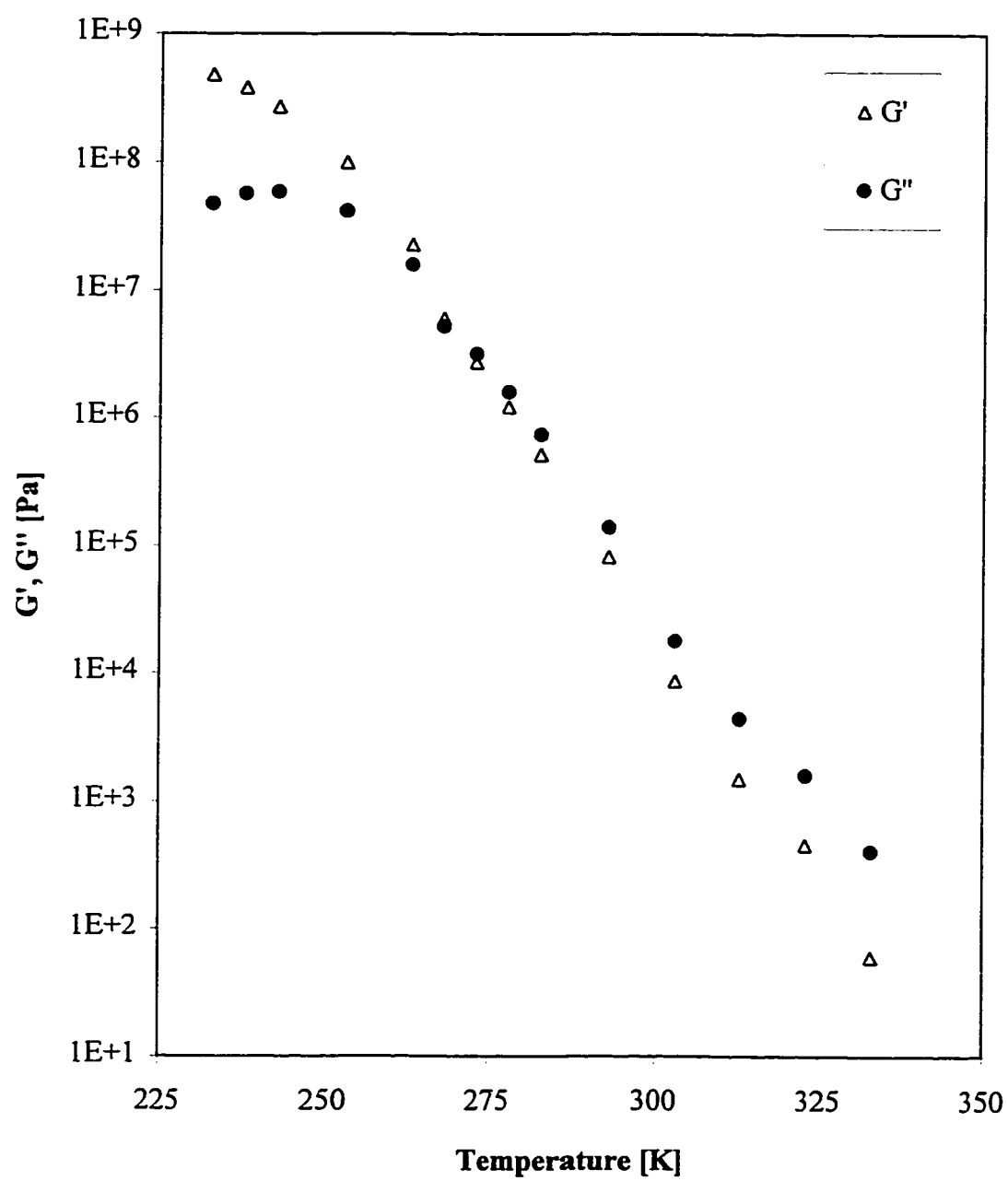


Figure 7.52 G' and G'' of Binder Modified with 5% Linear SBS at Frequency 0.1 Hz

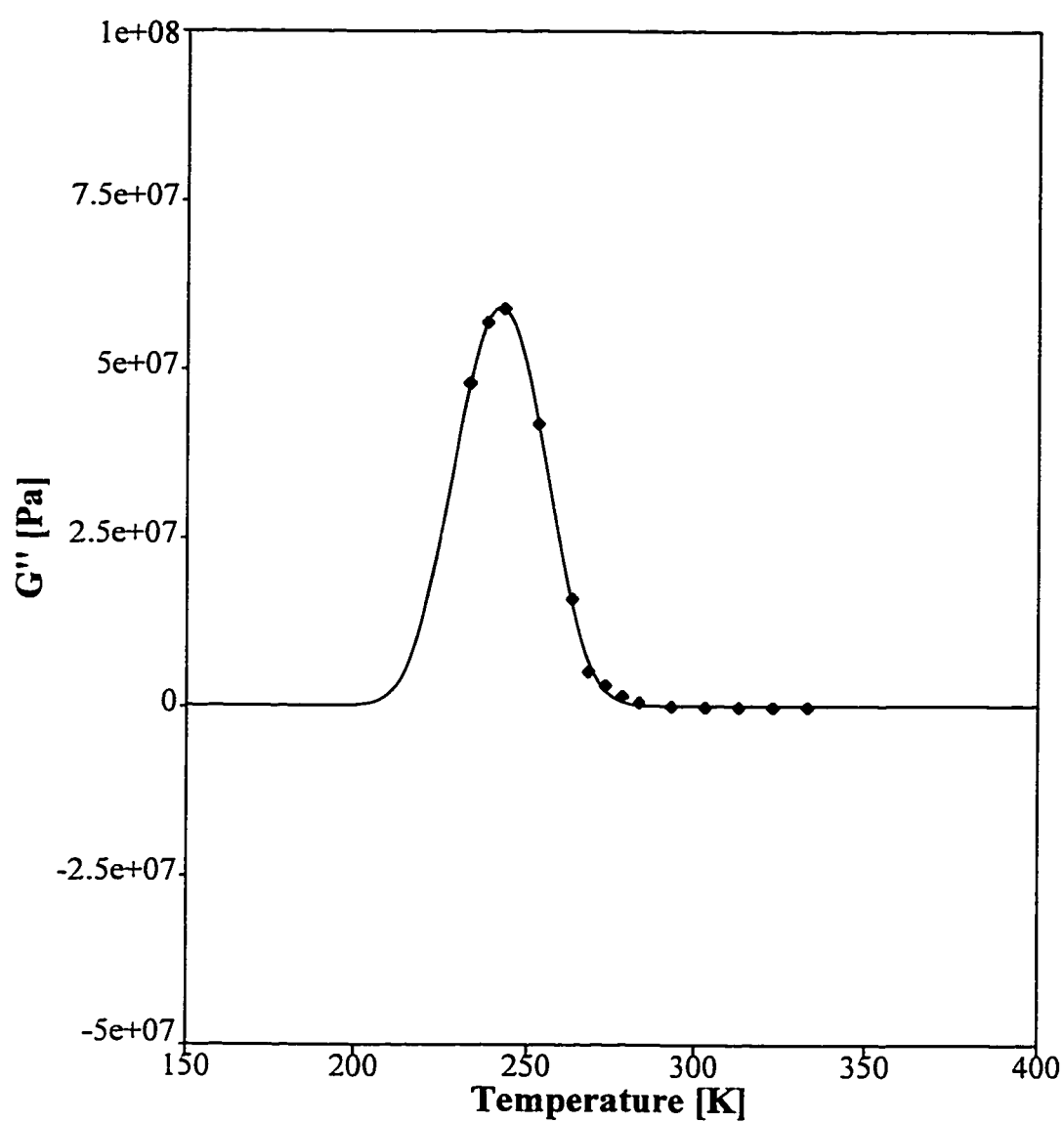


Figure 7.53 Peak Function of Binder Modified with 5% Linear SBS at Frequency 0.1 Hz

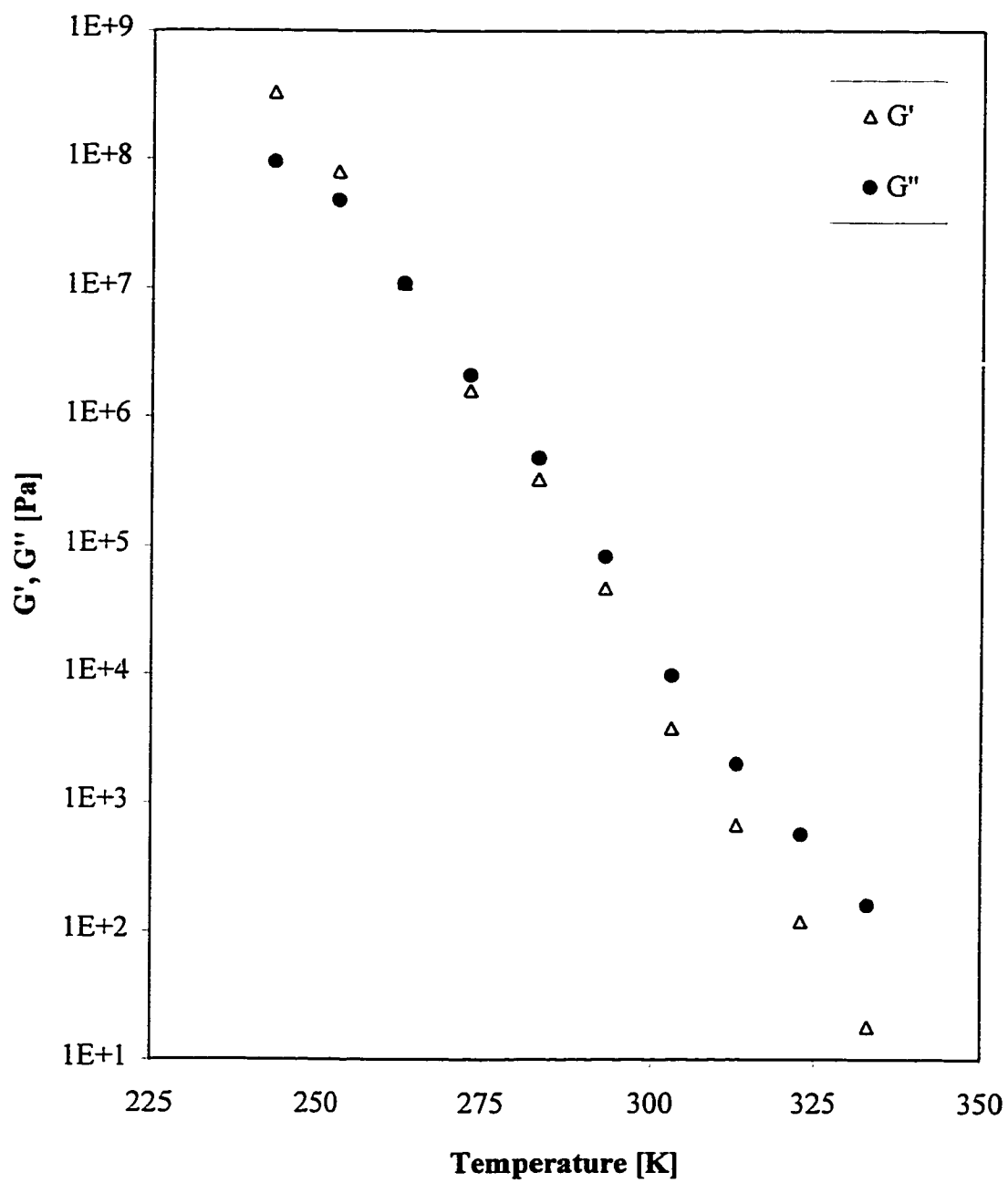


Figure 7.54 G' and G'' of Binder Modified with 5% EVA at Frequency 0.1 Hz

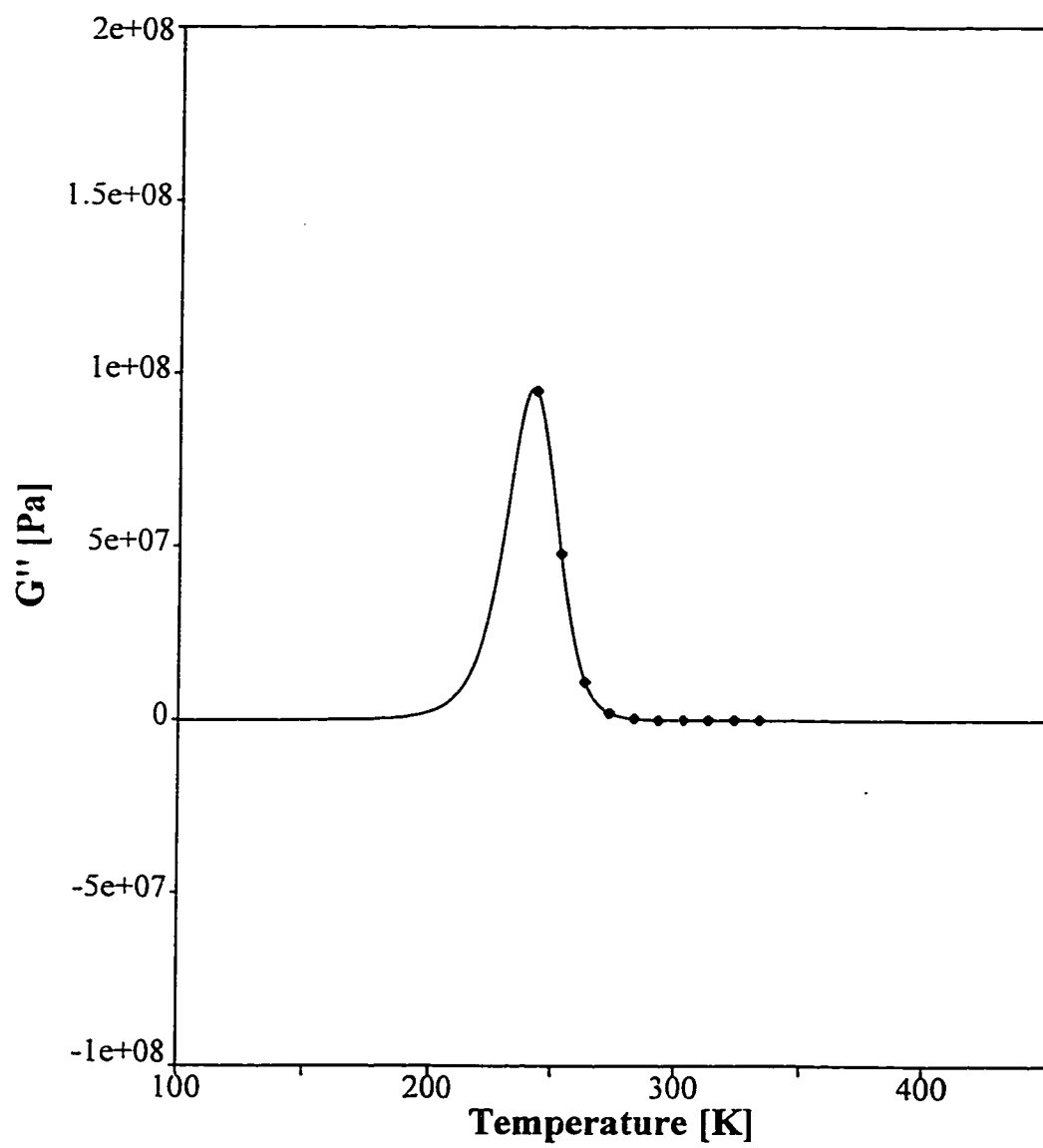


Figure 7.55 Peak Function of Binder Modified with 5% EVA (Elvax 350) at Frequency 0.1 Hz

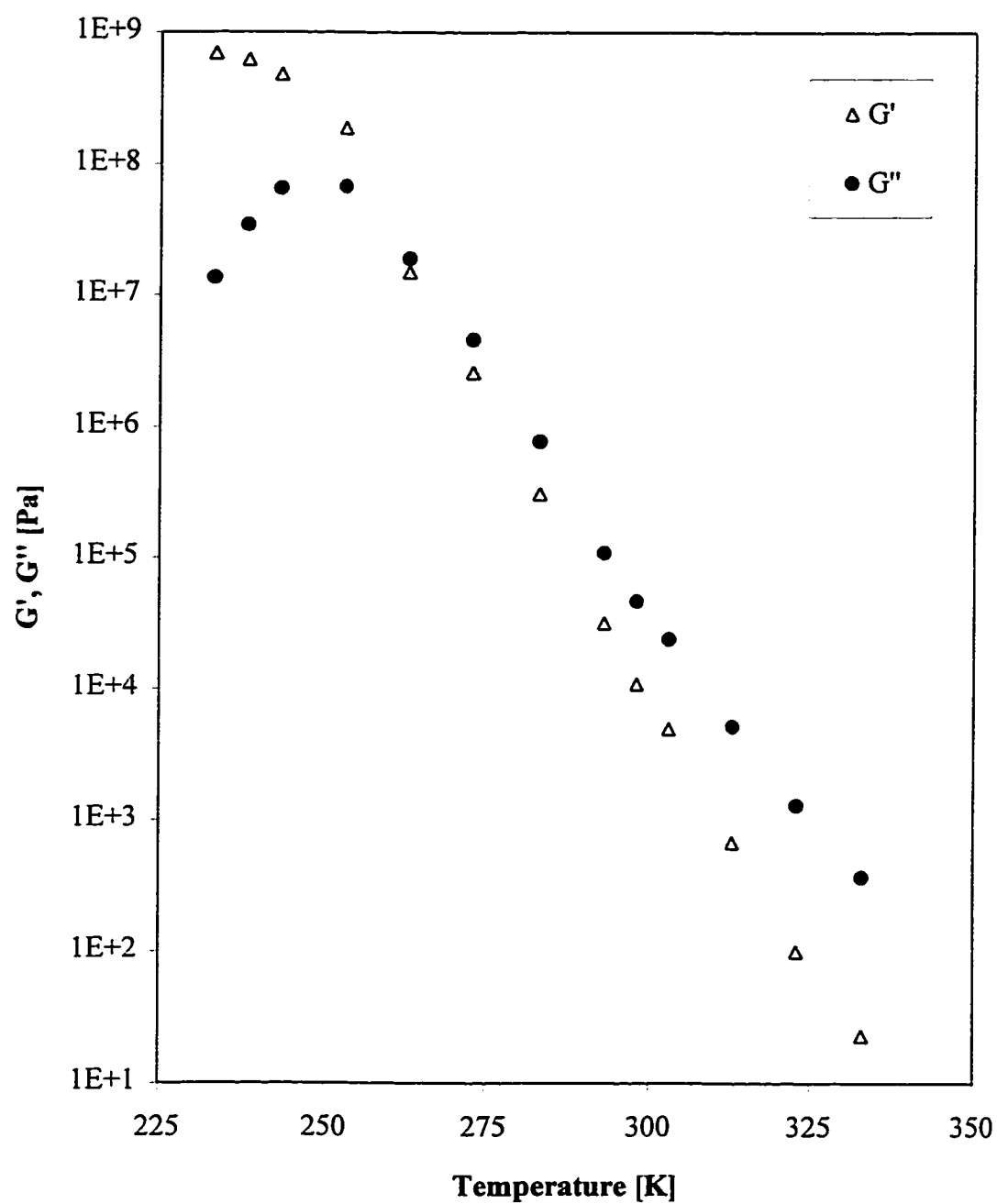


Figure 7.56 G' and G'' of Base Asphalt at Frequency 1 Hz

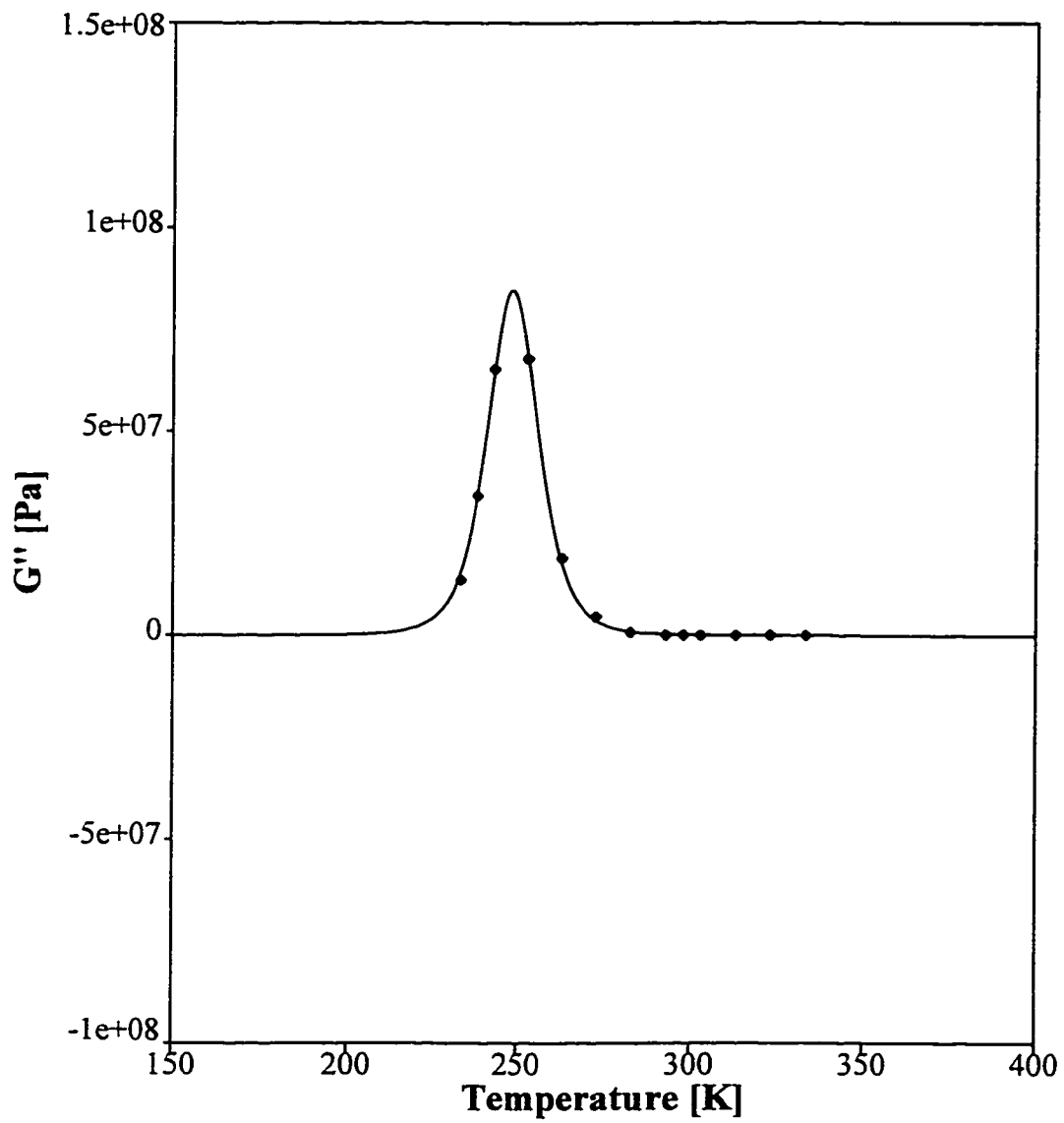


Figure 7.57 Peak Function of Base Asphalt at Frequency 1 Hz

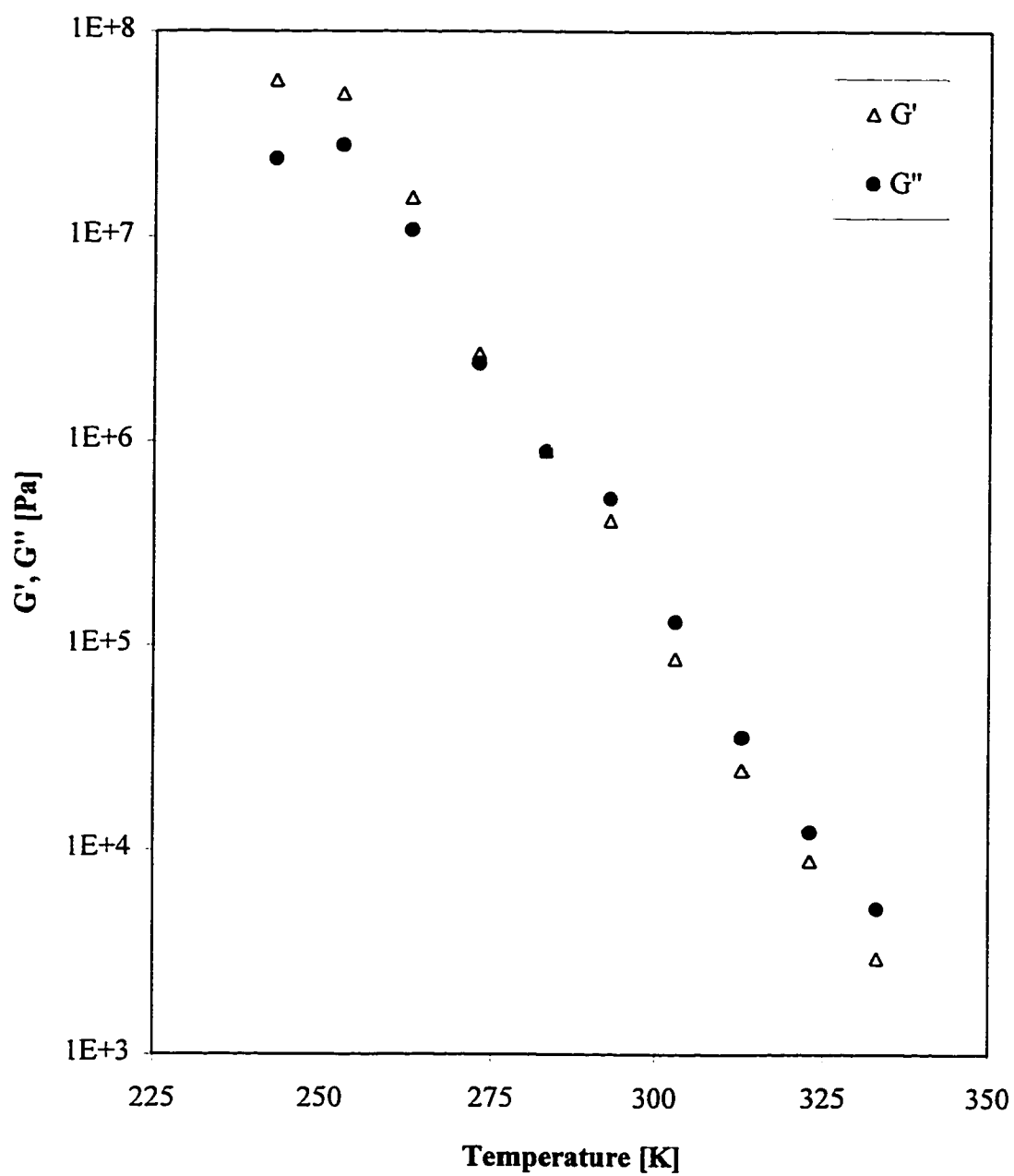


Figure 7.58 G' and G'' of Binder Modified with 5% Radial SBS at Frequency 1Hz

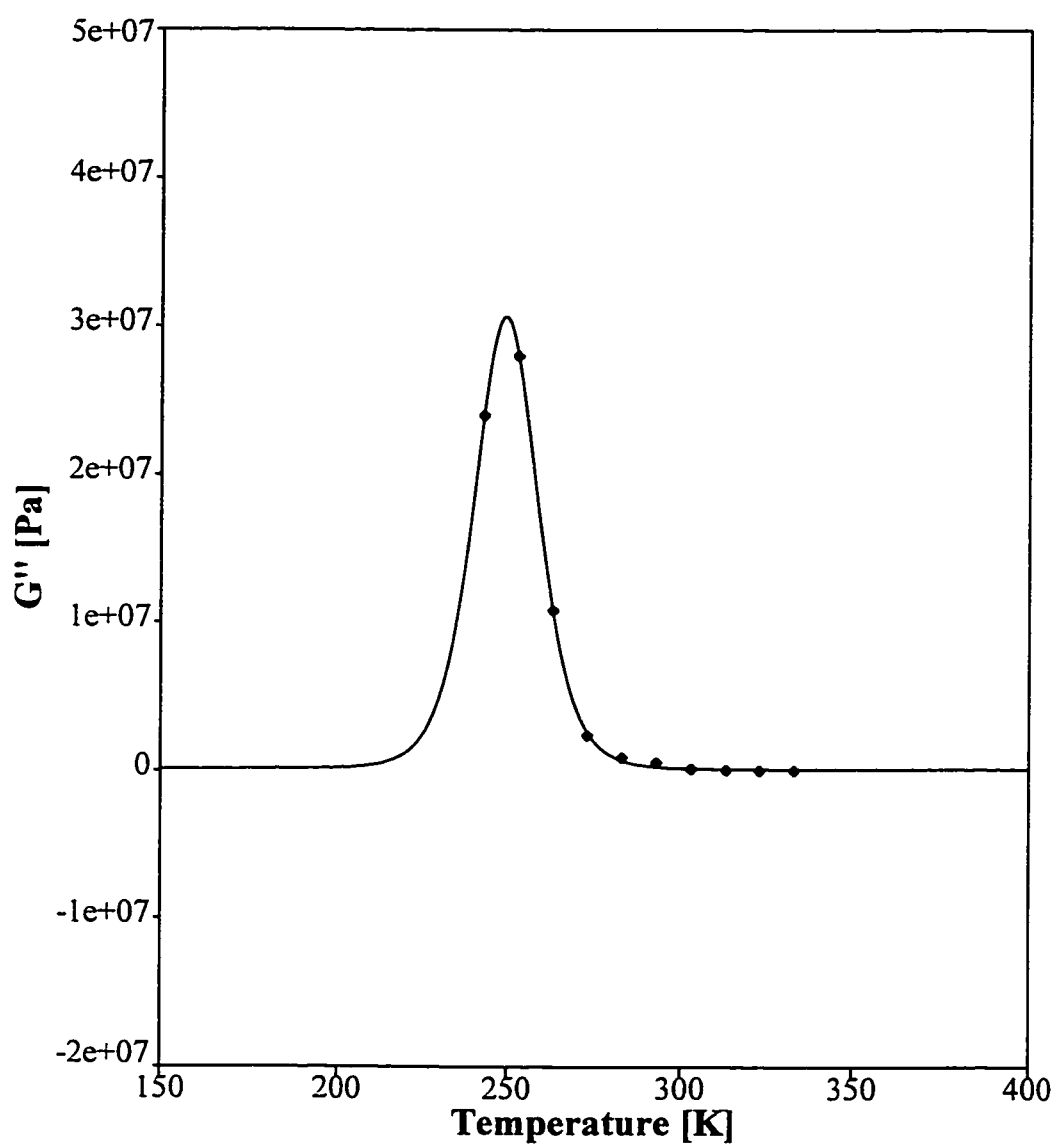


Figure 7.59 Peak Function of Binder Modified with 5% Radial SBS at Frequency 1 Hz

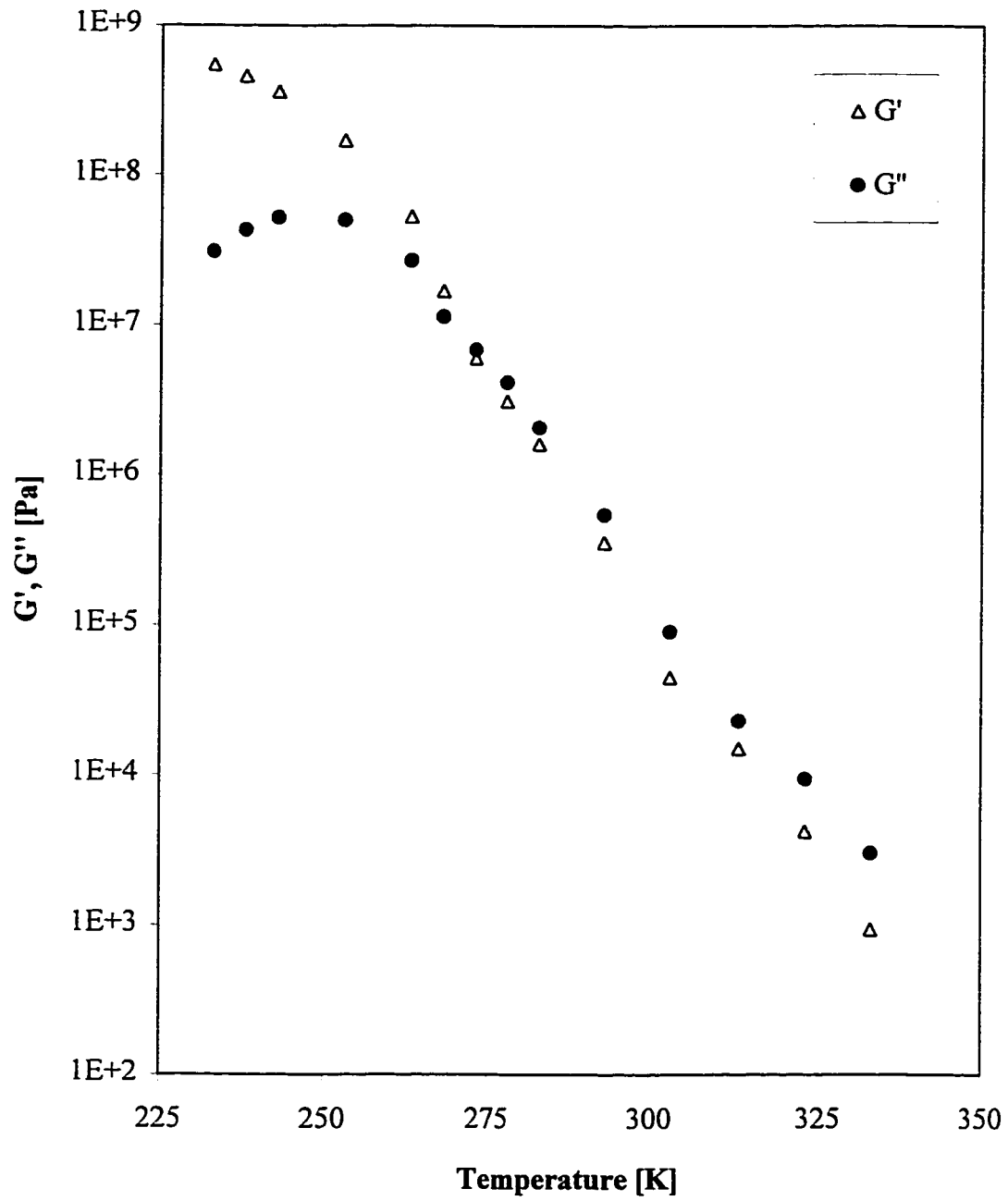


Figure 7.60 G' and G'' of Binder Modified with 5% Linear SBS at Frequency 1 Hz

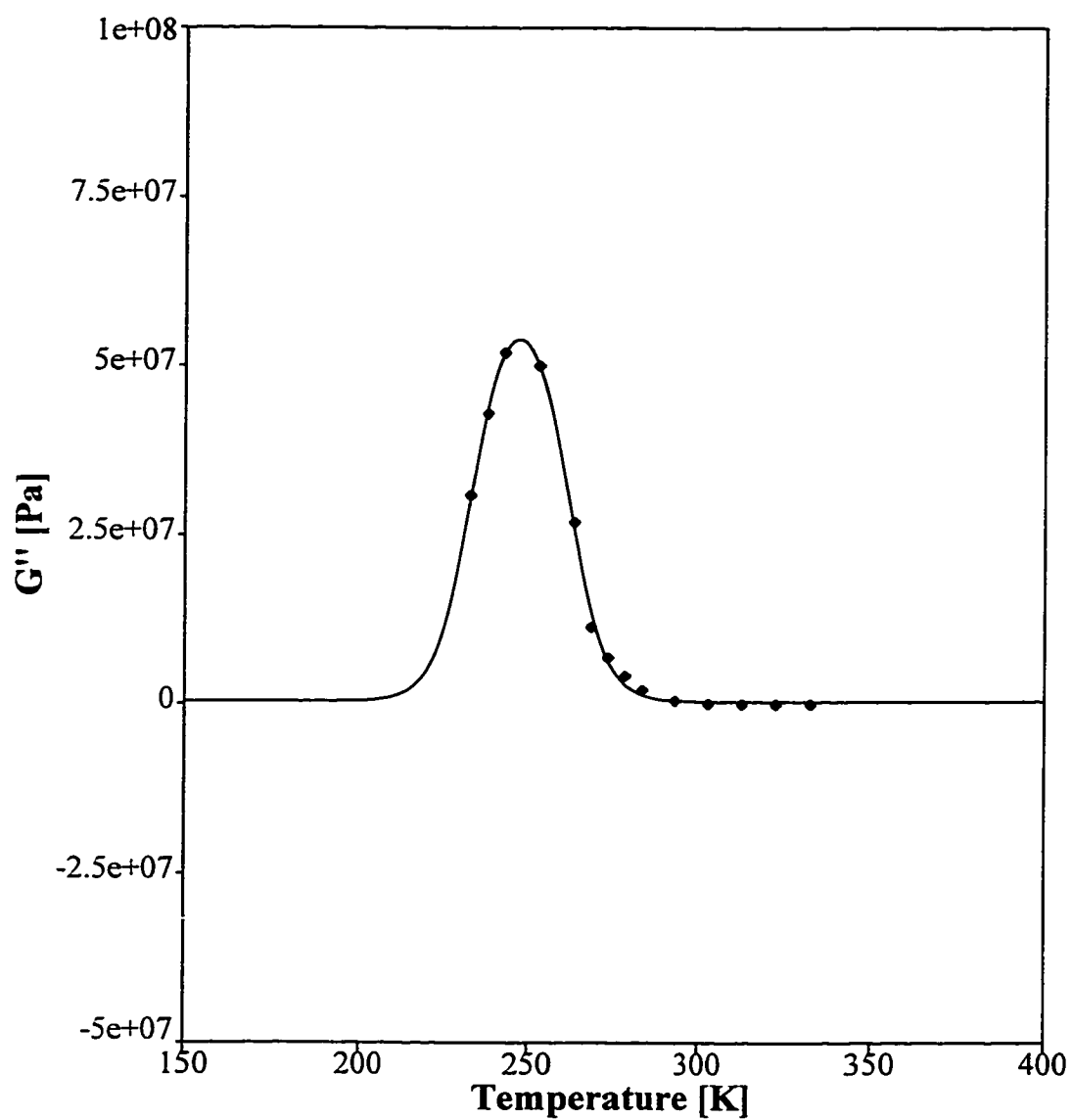


Figure 7.61 Peak Function of Binder Modified with 5% Linear SBS at Frequency 1 Hz

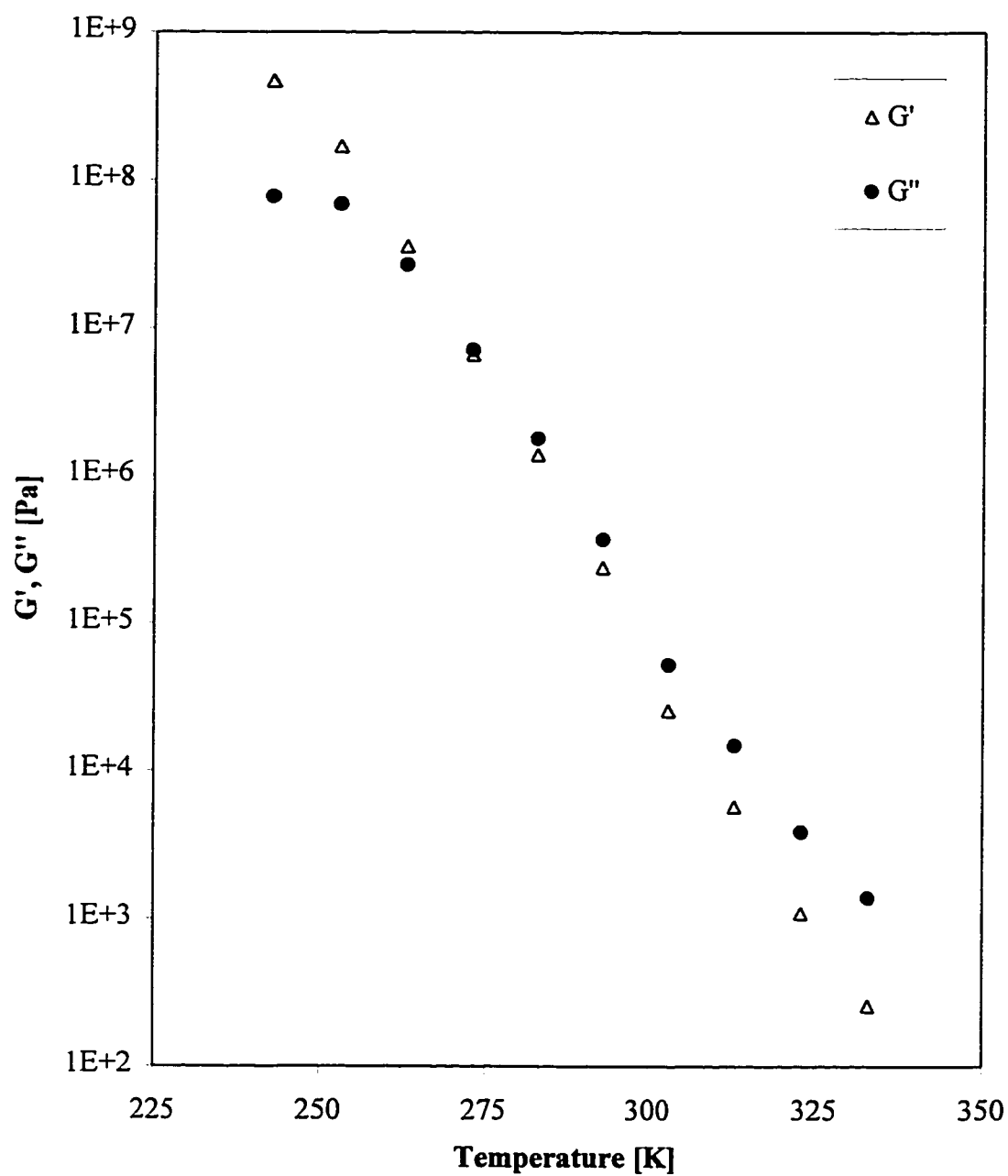


Figure 7.62 G' and G'' of Binder Modified with 5% EVA at Frequency 1 Hz

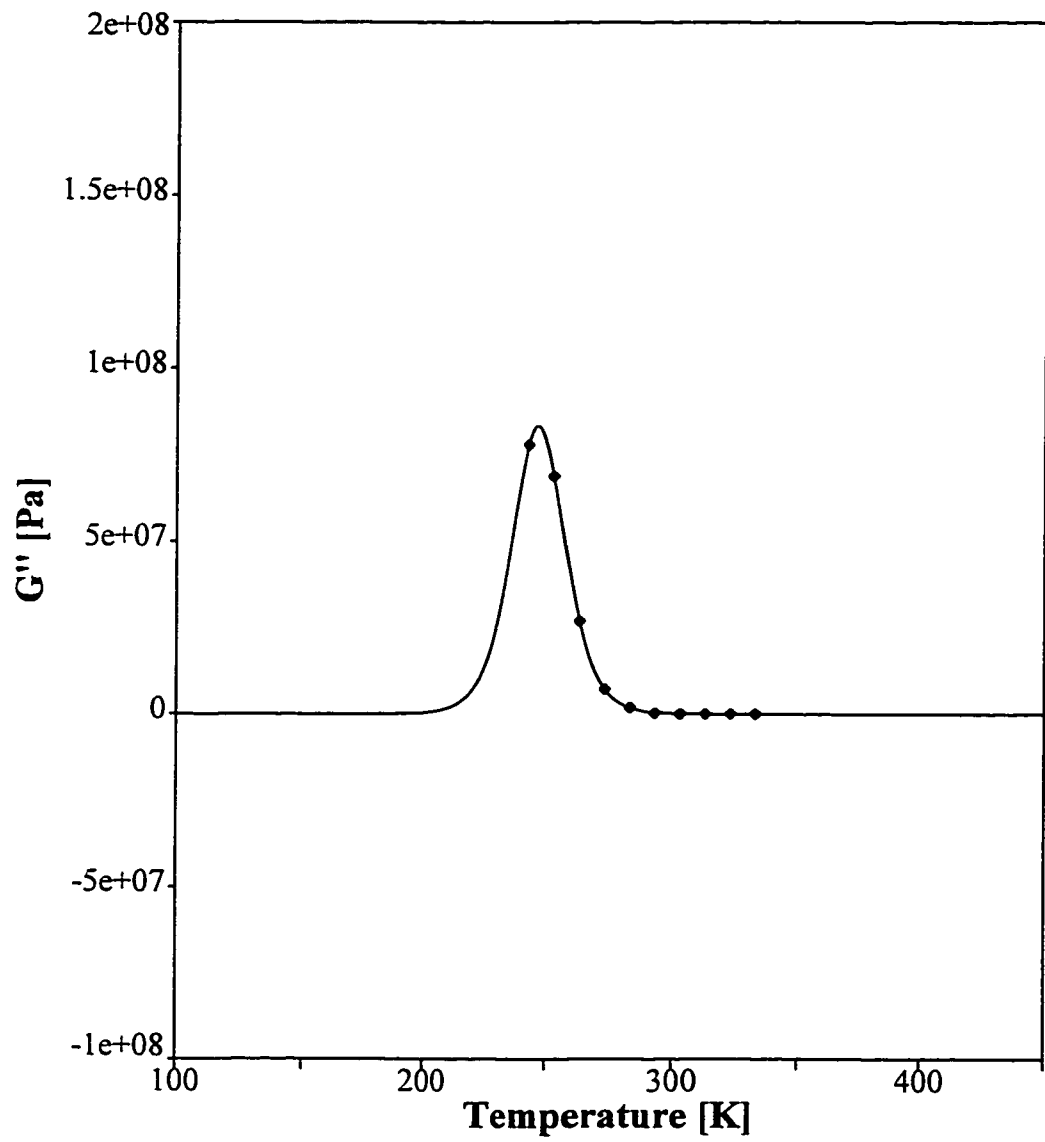


Figure 7.63 Peak Function of Binder Modified with 5% EVA (Elvax 350) at Frequency 1 Hz

CHAPTER 8

Conclusions and Recommendations

8.1 Conclusions

The purpose of this study was to conduct a comprehensive laboratory evaluation of the effects of several promising polymer modifiers on the physical properties of paving asphalts by conventional and SHRP (Strategic Highway Research Programs) binder tests, as well as on their rheological properties by using rheological measurements.

This work demonstrated the effectiveness of various polymers in improving the properties of asphalt, especially its high temperature properties. The appropriate choice of the base asphalt, polymer type, polymer concentration and methods of mixing determines the characteristics of the binders modified with polymers. The experimental results presented in Chapter 7 indicate that rheological measurements can be used as a powerful tool in the design and characterization of viscoelastic blends.

The main findings from this study are summarized as follows:

8.1.1 Internal Structure

Microscopy has been found to be a useful tool, which complements the rheological measurements. The judicious use of microscopy allows a deeper understanding of the underlying morphologies of modified binders. The compatibility between the asphalt and different polymers depends on many factors. The most important ones, as observed from microscopy, are the polymer microstructure and the consequences of thermal/mechanical history in dispersion of the polymer-modified asphalt binders.

- The microscopy shows that there can be a state of dispersion of polymer in asphalt, or at higher concentration of polymer dispersion of asphalt in polymer. This can be seen on pictures of rubber/asphalt with the amount of rubber over 5%.
- Materials with higher molecular weight tend to produce coarser dispersions.
- Plastics used in this study, never produced dispersion of asphalt in polymer. It might be because they do not swell by taking the oil from asphalt.

8.1.2 Mechanical Properties

8.1.2.1 Impact on High Service Temperature Behavior

All modifiers used in this study are effective in improving the binder properties at high pavement temperatures. This improvement increases with the increased the concentration of polymers. The increase of the highest service temperature should give the binders an improved resistance to permanent deformation. The binders modified with EVA polymers, Elvax 150W and Elvax 350, have less effect on the improvement of the resistance to permanent deformation compared with the binders modified with SBS and SIS polymers when measured before aging.

8.1.2.2 Impact on Low Service Temperature Behaviour

At low pavement temperature, the low service temperature properties measured by stiffness show tendency to worsen in most cases. Stiffness, however, does not fully describe the low temperature behaviour and tensile properties should be tested.

8.1.3 Durability

- The mass loss of binders modified with EVA is higher than the mass loss of the base asphalt as well as binders modified with SBS and SIS. This might be caused by higher absorption of light oils by SBS and SIS polymers. It, however, does not explain the mass loss higher than that of the base asphalt.
- All the maximum allowed high service temperatures, given by $G^*/\sin \delta$, of binders modified with the radial, linear SBS, and SIS polymers, after aging, are lower than those of binders before aging. On the contrary, the highest allowed service temperatures of binders modified with 3% and 5% EVA, Elvax 150W, 3% EVA, Elvax 350, after aging, are higher than those of binders before aging. The binders modified with low concentration of EVA polymers show more improved resistance to permanent deformation after the aging. This might be caused by larger mass loss of the binders modified with EVA polymers, especially at low concentrations, during the aging. The binders modified with low concentrations of EVA polymers turn harder than those modified with SBS and SIS polymers. One explanation of this fact might be the oxidative degradation of unsaturated butadiene and isoprene based polymers. Products of this degradation, occurring during RTFO test might soften the polymer/asphalt composition.
- The addition of SBS, SIS, and EVA increases the values of viscosity at 60 °C before aging, which is an indication of improved resistance against rutting of the pavement. These are proportional to the concentration of SBS, SIS, and EVA polymers. After aging, the viscosities of binders modified with polymers and the base asphalt are higher than those of binders before aging. The effects of aging can be seen from the aging index.
- Same trend has also been observed from the values of kinematic viscosity at 135 °C. From the above test, it is found that most of the binders modified with SBS, SIS, and EVA polymers can be used for the production of paving mixes with the existing

equipment, while the asphalt modified with 7% radial SBS, Finaprene 411, is probably an exception.

- The addition of SBS, SIS, and EVA polymers decreases the penetration values of the binders before and after RTFOT aging. The lower the molecular weight of SBS, the higher the penetration values are. The material with lower vinyl acetate and higher molecular weight of EVA produced harder polymer/asphalt blends. The binders modified with EVA polymers have poor resistance to oxidative hardening compared with the binders modified with SBS and SIS polymers according to their penetration ratios. This, might be either consequence of SBS and SIS polymers retaining the lighter oils from asphalt, or, again, the result of partial decomposition of unsaturated polymers (SBS, SIS), which compensates for the hardening of asphalt.

8.1.4 Rheology

- The time-temperature superposition is found to be valid over large temperature/frequency ranges for all binders modified with various polymers and base asphalt used in this work. Most of the binders need only horizontal shift, the exception is the binder modified with Elvax 350 which needs vertical shift, as well. The temperature dependency of the shift factor a_T obeys the WLF relationship in all cases.
- It has been found that the addition of polymers dramatically changes the properties of the binders at high temperatures or low rates of loading. It has been found that the loss tangent is the dynamic material function which is most sensitive to the type and amount of a modifying polymer. This has been correlated with varying degrees of success to permanent deformation in the asphalt mix.

- The glass transition temperatures of the base and modified binders, measured by dynamic mechanical analysis at 0.1 Hz frequency, are generally more sensitive to the composition of the tested materials, than those measured at 1 Hz frequency.

8.2 Recommendation

In order to further improve the physical and rheological properties of the binders, one could test various mixing conditions, choose different base asphalts, create more compatibility of asphalt/polymer. One particular interesting way is using a “cocktail” by mixing several different polymers into one base asphalt, for example, by blending low concentration of EVA and SBS polymers into the base asphalt simultaneously.

Although a large amount of testing has been done in this study, the overall testing results for various polymer modified asphalt are still limited. Further physical and rheological tests are required in order to fully understand the contribution of asphalt/polymer to the performance of mixes.

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APPENDIX – A**Performance Graded Asphalt Binder Specification**

Table A.1 : SUPERPAVE™ Grades

Performance Grade		PG-52										PG-58									
		-10	-16	-22	-28	-34	-40	-46	-52	-58	-64	-70	-76	-82	-88	-94	-100				
Average 7-day Max. Pavement Design Temp., °C		< 52										< 58									
Min. Pav. Design Temp., °C		>-10	>-16	>-22	>-28	>-34	>-40	>-46	>-52	>-58	>-64	>-70	>-76	>-82	>-88	>-94	>-100				
Flash Point Temp., °C		Original Binder										Original Binder									
Flash Point Temp., °C		230										230									
Viscosity, Max. 3.0 Pa.s, Test Temp., °C		135										135									
Dynamic Shear, G*/sinδ, Min. kPa, Test Temp. @10 rad/s, °C		52										58									
Mass Loss, Max. %		Rolling Thin Film Oven Test Residue										Rolling Thin Film Oven Test Residue									
Mass Loss, Max. %		1.0										1.0									
Dynamic Shear, G*/sinδ, Min. 2.2 kPa, Test Temp. @10 rad/s, °C		52										58									
PAV Aging Temp., °C		90										100									
Dynamic Shear, G*/sinδ, Max. 5000 kPa, Test Temp. @10 rad/s, °C		25	22	19	16	13	10	7	4	1	-2	-5	-8	-11	-14	-17	-20				
Creep stiffness, S, Max., 3x 10 ⁵ Pa, m-value, Min, 0.30 Test Temp., 60 sec, °C		0	-6	-12	-18	-24	-30	-36	-42	-48	-54	-60	-66	-72	-78	-84	-90				
Direct Tension, Failure Strain, Min, 1%, Test Temp, °C		0	-6	-12	-18	-24	-30	-36	-42	-48	-54	-60	-66	-72	-78	-84	-90				

APPENDIX - B

Dynamic Measurement Data

Table B. 1 Dynamic Measurement Data for Base Asphalt

Temperature [°C]	Frequency [rad/s]	G' [Pa]	G'' [Pa]
5	6.28E-02	1.03E+04	4.10E+04
5	9.42E-02	1.52E+04	5.82E+04
5	1.26E-01	2.02E+04	7.40E+04
5	1.88E-01	2.99E+04	1.04E+05
5	2.51E-01	3.93E+04	1.31E+05
5	3.14E-01	4.81E+04	1.55E+05
5	3.77E-01	5.67E+04	1.79E+05
5	4.40E-01	6.48E+04	2.02E+05
5	5.02E-01	7.35E+04	2.24E+05
5	5.65E-01	8.15E+04	2.45E+05
5	6.28E-01	8.97E+04	2.66E+05
5	9.42E-01	1.27E+05	3.65E+05
5	1.26E+00	1.63E+05	4.51E+05
5	1.88E+00	2.35E+05	6.07E+05
5	2.51E+00	2.99E+05	7.48E+05
5	3.14E+00	3.54E+05	8.72E+05
5	3.77E+00	4.09E+05	9.87E+05
5	4.40E+00	4.63E+05	1.10E+06
5	5.02E+00	5.16E+05	1.20E+06
5	5.65E+00	5.63E+05	1.30E+06
5	6.28E+00	6.12E+05	1.39E+06

Table B. 1 (Cont'd)

5	9.42E+00	8.50E+05	1.82E+06
5	1.26E+01	1.07E+06	2.23E+06
10	1.34E-02	2.70E+03	1.25E+04
10	2.01E-02	3.74E+03	1.75E+04
10	2.69E-02	5.19E+03	2.23E+04
10	4.02E-02	7.59E+03	3.13E+04
10	5.37E-02	1.01E+04	3.97E+04
10	6.71E-02	1.25E+04	4.78E+04
10	8.06E-02	1.48E+04	5.56E+04
10	9.41E-02	1.73E+04	6.31E+04
10	1.07E-01	1.96E+04	7.01E+04
10	1.21E-01	2.18E+04	7.70E+04
10	1.34E-01	2.41E+04	8.40E+04
10	2.01E-01	3.49E+04	1.16E+05
10	2.69E-01	4.52E+04	1.45E+05
10	4.02E-01	6.42E+04	2.00E+05
10	5.37E-01	8.40E+04	2.49E+05
10	6.71E-01	1.03E+05	2.96E+05
10	8.06E-01	1.19E+05	3.38E+05
10	9.41E-01	1.36E+05	3.79E+05
10	1.07E+00	1.52E+05	4.18E+05
10	1.21E+00	1.68E+05	4.57E+05
10	1.34E+00	1.83E+05	4.92E+05
10	2.01E+00	2.54E+05	6.58E+05
10	2.69E+00	3.19E+05	7.99E+05
20	7.84E-04	1.03E+02	9.92E+02
20	1.05E-03	1.52E+02	1.30E+03
20	1.56E-03	2.58E+02	1.88E+03

Table B. 1 (Cont'd)

20	2.09E-03	3.56E+02	2.43E+03
20	2.61E-03	4.57E+02	2.98E+03
20	3.14E-03	5.68E+02	3.52E+03
20	3.66E-03	6.84E+02	4.05E+03
20	4.18E-03	7.88E+02	4.53E+03
20	4.70E-03	8.95E+02	5.02E+03
20	5.22E-03	9.99E+02	5.50E+03
20	7.84E-03	1.59E+03	7.84E+03
20	1.05E-02	2.07E+03	1.00E+04
20	1.56E-02	3.10E+03	1.42E+04
20	2.09E-02	4.24E+03	1.81E+04
20	2.61E-02	5.13E+03	2.19E+04
20	3.14E-02	6.13E+03	2.54E+04
20	3.66E-02	7.10E+03	2.88E+04
20	4.18E-02	8.06E+03	3.22E+04
20	4.70E-02	8.92E+03	3.54E+04
20	5.22E-02	9.81E+03	3.86E+04
20	7.84E-02	1.42E+04	5.35E+04
20	1.05E-01	1.80E+04	6.76E+04
30	4.45E-05	1.72E+00	6.39E+01
30	6.67E-05	3.15E+00	9.49E+01
30	8.92E-05	5.16E+00	1.26E+02
30	1.33E-04	9.55E+00	1.87E+02
30	1.78E-04	1.44E+01	2.47E+02
30	2.22E-04	2.00E+01	3.06E+02
30	2.67E-04	2.58E+01	3.64E+02
30	3.12E-04	3.26E+01	4.21E+02
30	3.55E-04	3.86E+01	4.78E+02

Table B. 1 (Cont'd)

30	4.00E-04	4.52E+01	5.34E+02
30	4.45E-04	5.19E+01	5.91E+02
30	6.67E-04	8.79E+01	8.60E+02
30	8.92E-04	1.27E+02	1.13E+03
30	1.33E-03	2.07E+02	1.64E+03
30	1.78E-03	2.93E+02	2.13E+03
30	2.22E-03	3.80E+02	2.60E+03
30	2.67E-03	4.68E+02	3.06E+03
30	3.12E-03	5.53E+02	3.51E+03
30	3.55E-03	6.42E+02	3.95E+03
30	4.00E-03	7.40E+02	4.36E+03
30	4.45E-03	8.22E+02	4.84E+03
30	6.67E-03	1.29E+03	6.89E+03
30	8.92E-03	1.77E+03	8.85E+03
40	1.01E-05	8.71E-02	1.49E+01
40	1.35E-05	1.28E-01	1.98E+01
40	2.01E-05	3.71E-01	2.95E+01
40	2.69E-05	6.87E-01	3.95E+01
40	3.37E-05	1.01E+00	4.89E+01
40	4.04E-05	1.38E+00	5.87E+01
40	5.38E-05	2.45E+00	7.79E+01
40	6.05E-05	2.84E+00	8.76E+01
40	6.73E-05	3.34E+00	9.68E+01
40	1.01E-04	6.44E+00	1.44E+02
40	1.35E-04	9.50E+00	1.91E+02
40	2.01E-04	1.75E+01	2.81E+02
40	2.69E-04	2.60E+01	3.71E+02
40	3.37E-04	3.63E+01	4.58E+02

Table B. 1 (Cont'd)

40	4.04E-04	4.52E+01	5.45E+02
40	4.72E-04	5.50E+01	6.29E+02
40	5.38E-04	6.55E+01	7.13E+02
40	6.05E-04	7.71E+01	7.97E+02
40	6.73E-04	8.58E+01	8.76E+02
40	1.01E-03	1.42E+02	1.28E+03
40	1.35E-03	2.00E+02	1.67E+03
45	2.30E-05	4.49E-01	3.27E+01
45	2.56E-05	6.39E-01	3.61E+01
45	5.13E-05	2.16E+00	7.17E+01
45	7.66E-05	4.27E+00	1.06E+02
45	1.02E-04	6.39E+00	1.41E+02
45	1.28E-04	8.96E+00	1.75E+02
45	1.54E-04	1.16E+01	2.08E+02
45	1.79E-04	1.45E+01	2.41E+02
45	2.05E-04	1.70E+01	2.76E+02
45	2.30E-04	2.10E+01	3.08E+02
45	2.56E-04	2.37E+01	3.39E+02
45	3.84E-04	4.02E+01	5.00E+02
45	5.13E-04	5.70E+01	6.53E+02

Table B. 2 Dynamic Measurement Data for Binder Modified with 3% Radial SBS, (Finaprene 411)

Temperature [°C]	Frequency [rad/s]	G' [Pa]	G'' [Pa]
5	1.26E-01	8.27E+04	1.67E+05
5	1.89E-01	1.12E+05	2.18E+05
5	2.51E-01	1.35E+05	2.63E+05
5	3.14E-01	1.59E+05	3.07E+05
5	3.77E-01	1.83E+05	3.45E+05
5	4.40E-01	2.02E+05	3.78E+05
5	5.03E-01	2.26E+05	4.13E+05
5	5.65E-01	2.43E+05	4.44E+05
5	6.28E-01	2.61E+05	4.73E+05
5	9.42E-01	3.45E+05	6.12E+05
5	1.26E+00	4.16E+05	7.21E+05
5	1.89E+00	5.21E+05	9.21E+05
5	2.51E+00	6.41E+05	1.09E+06
5	3.14E+00	7.28E+05	1.22E+06
5	3.77E+00	8.32E+05	1.35E+06
5	4.40E+00	9.19E+05	1.46E+06
5	5.03E+00	1.00E+06	1.60E+06
5	5.65E+00	1.09E+06	1.71E+06
5	6.28E+00	1.17E+06	1.82E+06
5	9.42E+00	1.54E+06	2.31E+06
5	1.26E+01	1.95E+06	2.71E+06
10	2.75E-02	2.88E+04	6.13E+04
10	4.12E-02	3.89E+04	8.11E+04
10	5.50E-02	4.72E+04	9.88E+04
10	6.87E-02	5.57E+04	1.16E+05

Table B. 2 (Cont'd)

10	8.25E-02	6.45E+04	1.31E+05
10	9.62E-02	7.23E+04	1.46E+05
10	1.10E-01	7.93E+04	1.60E+05
10	1.24E-01	8.69E+04	1.73E+05
10	1.37E-01	9.36E+04	1.85E+05
10	2.06E-01	1.24E+05	2.45E+05
10	2.75E-01	1.53E+05	2.93E+05
10	4.12E-01	1.96E+05	3.79E+05
10	5.50E-01	2.43E+05	4.56E+05
10	6.87E-01	2.82E+05	5.21E+05
10	8.25E-01	3.20E+05	5.75E+05
10	9.62E-01	3.51E+05	6.29E+05
10	1.10E+00	3.90E+05	6.83E+05
10	1.24E+00	4.16E+05	7.33E+05
10	1.37E+00	4.44E+05	7.78E+05
10	2.06E+00	5.68E+05	9.76E+05
10	2.75E+00	6.63E+05	1.13E+06
20	2.97E-03	5.75E+03	1.25E+04
20	3.30E-03	6.21E+03	1.36E+04
20	4.95E-03	8.14E+03	1.80E+04
20	6.59E-03	1.01E+04	2.23E+04
20	9.89E-03	1.38E+04	3.00E+04
20	1.32E-02	1.70E+04	3.65E+04
20	1.65E-02	2.00E+04	4.29E+04
20	1.98E-02	2.24E+04	4.86E+04
20	2.31E-02	2.55E+04	5.39E+04
20	2.64E-02	2.78E+04	5.91E+04
20	2.97E-02	3.03E+04	6.42E+04

Table B. 2 (Cont'd)

20	3.30E-02	3.26E+04	6.88E+04
20	4.95E-02	4.35E+04	9.03E+04
20	6.59E-02	5.18E+04	1.09E+05
30	9.08E-05	2.61E+02	9.93E+02
30	1.36E-04	4.08E+02	1.39E+03
30	1.82E-04	5.51E+02	1.73E+03
30	2.73E-04	8.28E+02	2.36E+03
30	3.63E-04	1.09E+03	2.92E+03
30	4.54E-04	1.36E+03	3.44E+03
30	5.45E-04	1.59E+03	3.89E+03
30	6.36E-04	1.84E+03	4.37E+03
30	7.27E-04	2.05E+03	4.79E+03
30	8.17E-04	2.23E+03	5.19E+03
30	9.08E-04	2.43E+03	5.60E+03
30	1.36E-03	3.33E+03	7.45E+03
30	1.82E-03	4.10E+03	9.13E+03
30	2.73E-03	5.40E+03	1.24E+04
30	3.63E-03	6.79E+03	1.52E+04
30	4.54E-03	7.92E+03	1.78E+04
30	5.45E-03	9.10E+03	2.02E+04
30	6.36E-03	1.03E+04	2.27E+04
30	7.27E-03	1.13E+04	2.50E+04
30	8.17E-03	1.21E+04	2.73E+04
30	9.08E-03	1.32E+04	2.95E+04
30	1.36E-02	1.79E+04	3.97E+04
30	1.82E-02	2.23E+04	4.90E+04
40	1.14E-05	2.10E+01	1.67E+02
40	1.72E-05	3.54E+01	2.42E+02

Table B. 2 (Cont'd)

40	2.29E-05	5.03E+01	3.13E+02
40	3.43E-05	8.32E+01	4.49E+02
40	4.57E-05	1.21E+02	5.79E+02
40	5.72E-05	1.57E+02	6.99E+02
40	6.86E-05	1.96E+02	8.14E+02
40	8.00E-05	2.35E+02	9.23E+02
40	9.15E-05	2.73E+02	1.03E+03
40	1.03E-04	3.14E+02	1.13E+03
40	1.14E-04	3.54E+02	1.23E+03
40	1.72E-04	5.30E+02	1.69E+03
40	2.29E-04	7.17E+02	2.10E+03
40	3.43E-04	1.07E+03	2.82E+03
40	4.57E-04	1.36E+03	3.48E+03
40	5.72E-04	1.66E+03	4.09E+03
40	6.86E-04	1.91E+03	4.68E+03
40	8.00E-04	2.19E+03	5.19E+03
40	9.15E-04	2.41E+03	5.74E+03
40	1.03E-03	2.65E+03	6.22E+03
40	1.14E-03	2.86E+03	6.73E+03
40	1.72E-03	3.90E+03	9.04E+03
40	2.29E-03	4.83E+03	1.12E+04
50	3.88E-06	5.53E+00	5.87E+01
50	7.77E-06	1.24E+01	1.13E+02
50	9.71E-06	1.65E+01	1.40E+02
50	1.17E-05	2.09E+01	1.65E+02
50	1.36E-05	2.53E+01	1.91E+02
50	1.55E-05	2.99E+01	2.16E+02
50	1.75E-05	3.56E+01	2.40E+02

Table B. 2 (Cont'd)

50	1.94E-05	4.00E+01	2.64E+02
50	2.91E-05	6.64E+01	3.79E+02
50	3.88E-05	9.64E+01	4.89E+02
50	5.83E-05	1.55E+02	6.93E+02
50	7.77E-05	2.19E+02	8.81E+02
50	9.71E-05	2.84E+02	1.06E+03
50	1.17E-04	3.46E+02	1.22E+03
50	1.36E-04	4.08E+02	1.38E+03
50	1.55E-04	4.70E+02	1.53E+03
50	1.75E-04	5.34E+02	1.67E+03
50	1.94E-04	5.88E+02	1.82E+03
50	2.91E-04	8.63E+02	2.46E+03
50	3.88E-04	1.12E+03	3.04E+03
60	7.57E-07	7.60E-01	1.29E+01
60	1.14E-06	1.28E+00	1.90E+01
60	1.51E-06	1.87E+00	2.49E+01
60	1.89E-06	2.48E+00	3.06E+01
60	2.27E-06	3.11E+00	3.64E+01
60	2.65E-06	3.66E+00	4.20E+01
60	5.68E-06	8.69E+00	8.67E+01
60	7.57E-06	1.24E+01	1.14E+02
60	1.14E-05	2.10E+01	1.65E+02
60	1.51E-05	2.98E+01	2.16E+02
60	1.89E-05	3.97E+01	2.64E+02
60	2.27E-05	4.98E+01	3.11E+02
60	2.65E-05	6.04E+01	3.56E+02
60	3.03E-05	7.16E+01	4.02E+02
60	3.41E-05	8.20E+01	4.43E+02

Table B. 2 (Cont'd)

60	3.79E-05	9.32E+01	4.88E+02
60	5.68E-05	1.53E+02	6.89E+02
60	7.57E-05	2.13E+02	8.76E+02

Table B. 3 Dynamic Measurement Data for Binder Modified with 5% Radial SBS, (Finaprene 411)

Temperature [°C]	Frequency [rad/s]	G' [Pa]	G'' [Pa]
70	1.90E-07	1.17E+01	2.91E+01
70	2.85E-07	1.48E+01	4.23E+01
70	3.79E-07	1.76E+01	5.18E+01
70	5.69E-07	2.24E+01	7.05E+01
70	9.49E-07	3.22E+01	1.06E+02
70	1.14E-06	3.74E+01	1.22E+02
70	1.33E-06	4.14E+01	1.38E+02
70	1.52E-06	4.65E+01	1.53E+02
70	1.71E-06	5.06E+01	1.68E+02
70	1.90E-06	5.49E+01	1.83E+02
70	2.85E-06	7.60E+01	2.56E+02
70	3.79E-06	9.93E+01	3.24E+02
70	5.69E-06	1.40E+02	4.48E+02
70	7.59E-06	1.81E+02	5.61E+02
70	9.49E-06	2.25E+02	6.70E+02
70	1.14E-05	2.62E+02	7.72E+02
70	1.33E-05	3.02E+02	8.70E+02
70	1.52E-05	3.42E+02	9.62E+02
70	1.71E-05	3.79E+02	1.05E+03
70	1.90E-05	4.18E+02	1.14E+03
60	2.45E-05	5.19E+02	1.34E+03
50	2.82E-05	6.02E+02	1.52E+03
70	2.85E-05	6.07E+02	1.54E+03
50	3.52E-05	7.41E+02	1.80E+03
60	3.68E-05	7.45E+02	1.83E+03

Table B. 3 (Cont'd)

70	3.79E-05	7.85E+02	1.90E+03
50	4.23E-05	8.68E+02	2.04E+03
40	4.77E-05	1.02E+03	2.33E+03
60	4.90E-05	9.73E+02	2.25E+03
50	4.93E-05	1.00E+03	2.30E+03
50	5.64E-05	1.13E+03	2.53E+03
60	6.13E-05	1.18E+03	2.65E+03
50	6.34E-05	1.24E+03	2.74E+03
50	7.05E-05	1.35E+03	2.96E+03
40	7.15E-05	1.31E+03	2.92E+03
60	7.35E-05	1.37E+03	3.00E+03
60	8.57E-05	1.59E+03	3.33E+03
40	9.53E-05	1.70E+03	3.60E+03
60	9.80E-05	1.77E+03	3.65E+03
50	1.06E-04	1.93E+03	3.90E+03
60	1.10E-04	1.95E+03	3.96E+03
60	1.23E-04	2.13E+03	4.24E+03
50	1.41E-04	2.45E+03	4.73E+03
40	1.43E-04	2.41E+03	4.76E+03
60	1.84E-04	2.96E+03	5.51E+03
40	1.91E-04	3.10E+03	5.70E+03
50	2.12E-04	3.33E+03	6.22E+03
40	2.38E-04	3.67E+03	6.54E+03
60	2.45E-04	3.65E+03	6.61E+03
50	2.82E-04	4.23E+03	7.44E+03
40	2.86E-04	4.23E+03	7.36E+03
40	3.34E-04	4.82E+03	8.06E+03
50	3.52E-04	4.98E+03	8.48E+03

Table B. 3 (Cont'd)

40	3.81E-04	5.35E+03	8.76E+03
50	4.23E-04	5.76E+03	9.41E+03
40	4.29E-04	5.80E+03	9.38E+03
40	4.77E-04	6.28E+03	9.96E+03
50	4.93E-04	6.39E+03	1.03E+04
50	5.64E-04	7.08E+03	1.12E+04
50	6.34E-04	7.59E+03	1.21E+04
50	7.05E-04	8.20E+03	1.28E+04
40	7.15E-04	8.10E+03	1.28E+04
40	9.53E-04	9.95E+03	1.50E+04
50	1.06E-03	1.06E+04	1.64E+04
50	1.41E-03	1.27E+04	1.92E+04
40	1.43E-03	1.29E+04	1.86E+04
40	1.91E-03	1.52E+04	2.21E+04
40	2.38E-03	1.75E+04	2.53E+04
40	2.86E-03	1.93E+04	2.86E+04
40	3.34E-03	2.12E+04	3.14E+04
20	3.38E-03	2.16E+04	3.19E+04
40	3.81E-03	2.27E+04	3.38E+04
40	4.29E-03	2.44E+04	3.64E+04
40	4.77E-03	2.58E+04	3.89E+04
20	5.07E-03	2.68E+04	4.08E+04
20	6.76E-03	3.11E+04	4.99E+04
40	7.15E-03	3.22E+04	5.09E+04
20	8.45E-03	3.60E+04	5.84E+04
40	9.53E-03	3.82E+04	6.16E+04
20	1.01E-02	4.05E+04	6.54E+04
20	1.18E-02	4.44E+04	7.30E+04

Table B. 3 (Cont'd)

20	1.35E-02	4.80E+04	7.97E+04
20	1.52E-02	5.17E+04	8.62E+04
20	1.69E-02	5.50E+04	9.23E+04
20	2.54E-02	7.14E+04	1.22E+05
10	3.23E-02	8.40E+04	1.43E+05
20	3.38E-02	8.58E+04	1.47E+05
10	4.85E-02	1.10E+05	1.85E+05
10	6.46E-02	1.30E+05	2.22E+05
20	6.76E-02	1.34E+05	2.34E+05
10	8.07E-02	1.52E+05	2.59E+05
20	8.45E-02	1.54E+05	2.69E+05
5	9.42E-02	1.62E+05	2.78E+05
10	9.69E-02	1.73E+05	2.88E+05
20	1.01E-01	1.73E+05	2.99E+05
10	1.13E-01	1.89E+05	3.16E+05
20	1.18E-01	1.94E+05	3.31E+05
5	1.26E-01	1.95E+05	3.31E+05
10	1.29E-01	2.11E+05	3.43E+05
20	1.35E-01	2.07E+05	3.59E+05
10	1.45E-01	2.25E+05	3.69E+05
20	1.52E-01	2.26E+05	3.86E+05
10	1.62E-01	2.40E+05	3.93E+05
20	1.69E-01	2.40E+05	4.13E+05
5	1.89E-01	2.54E+05	4.33E+05
10	2.42E-01	3.13E+05	5.04E+05
5	2.51E-01	3.12E+05	5.18E+05
20	2.54E-01	3.10E+05	5.26E+05
5	3.14E-01	3.68E+05	5.86E+05

Table B. 3 (Cont'd)

10	3.23E-01	3.73E+05	5.93E+05
20	3.38E-01	3.72E+05	6.24E+05
5	3.77E-01	4.02E+05	6.43E+05
5	4.40E-01	4.43E+05	7.04E+05
10	4.85E-01	4.68E+05	7.67E+05
5	5.03E-01	4.77E+05	7.53E+05
5	5.65E-01	5.23E+05	8.10E+05
5	6.28E-01	5.54E+05	8.59E+05
10	6.46E-01	5.72E+05	9.00E+05
10	8.07E-01	6.46E+05	1.02E+06
5	9.42E-01	6.81E+05	1.09E+06
10	9.69E-01	7.14E+05	1.11E+06
10	1.13E+00	7.82E+05	1.20E+06
5	1.26E+00	8.30E+05	1.27E+06
10	1.29E+00	8.55E+05	1.30E+06
10	1.45E+00	9.17E+05	1.39E+06
10	1.62E+00	9.77E+05	1.48E+06
5	1.89E+00	1.11E+06	1.60E+06
10	2.42E+00	1.29E+06	1.87E+06
5	2.51E+00	1.26E+06	1.87E+06
5	3.14E+00	1.52E+06	2.15E+06
10	3.23E+00	1.59E+06	2.23E+06
5	3.77E+00	1.67E+06	2.38E+06
5	4.40E+00	1.85E+06	2.57E+06
5	5.03E+00	2.07E+06	2.75E+06
5	5.65E+00	2.22E+06	2.96E+06
5	6.28E+00	2.38E+06	3.09E+06
5	9.42E+00	3.11E+06	3.87E+06

Table B. 4 Dynamic Measurement Data for Binder Modified with 3% Linear SBS, (Kraton D1102)

Temperature [°C]	Frequency [rad/s]	G' [Pa]	G'' [Pa]
5	9.42E-02	2.05E+04	4.92E+04
5	1.26E-01	2.64E+04	6.25E+04
5	1.89E-01	3.62E+04	8.46E+04
5	2.51E-01	4.53E+04	1.06E+05
5	3.14E-01	5.54E+04	1.25E+05
5	3.77E-01	6.38E+04	1.42E+05
5	4.40E-01	7.31E+04	1.60E+05
5	5.03E-01	8.11E+04	1.75E+05
5	5.65E-01	8.86E+04	1.91E+05
5	6.28E-01	9.58E+04	2.06E+05
5	9.42E-01	1.33E+05	2.72E+05
5	1.26E+00	1.65E+05	3.32E+05
5	1.89E+00	2.26E+05	4.44E+05
5	2.51E+00	2.84E+05	5.30E+05
5	3.14E+00	3.35E+05	6.12E+05
5	3.77E+00	3.82E+05	6.93E+05
5	4.40E+00	4.27E+05	7.56E+05
5	5.03E+00	4.75E+05	8.23E+05
5	5.65E+00	5.12E+05	8.88E+05
5	6.28E+00	5.54E+05	9.46E+05
5	9.42E+00	7.30E+05	1.21E+06
5	1.26E+01	9.08E+05	1.43E+06
10	9.29E-03	4.38E+03	1.07E+04
10	1.39E-02	5.91E+03	1.41E+04
10	1.86E-02	6.99E+03	1.68E+04

Table B. 4 (Cont'd)

10	2.79E-02	9.46E+03	2.31E+04
10	3.72E-02	1.18E+04	2.86E+04
10	4.65E-02	1.43E+04	3.35E+04
10	5.58E-02	1.59E+04	3.78E+04
10	6.50E-02	1.82E+04	4.24E+04
10	7.43E-02	1.99E+04	4.64E+04
10	8.36E-02	2.16E+04	5.06E+04
10	9.29E-02	2.35E+04	5.49E+04
10	1.39E-01	3.13E+04	7.30E+04
10	1.86E-01	3.91E+04	9.01E+04
10	2.79E-01	5.39E+04	1.20E+05
10	3.72E-01	6.59E+04	1.46E+05
10	4.65E-01	7.85E+04	1.70E+05
10	5.58E-01	8.97E+04	1.94E+05
10	6.50E-01	1.01E+05	2.14E+05
10	7.43E-01	1.12E+05	2.35E+05
10	8.36E-01	1.21E+05	2.55E+05
10	9.29E-01	1.31E+05	2.73E+05
10	1.39E+00	1.74E+05	3.53E+05
10	1.86E+00	2.11E+05	4.23E+05
20	1.90E-04	1.54E+02	5.86E+02
20	2.85E-04	2.49E+02	8.01E+02
20	3.79E-04	3.21E+02	9.88E+02
20	5.69E-04	4.74E+02	1.35E+03
20	7.59E-04	6.23E+02	1.67E+03
20	9.49E-04	7.54E+02	1.95E+03
20	1.14E-03	8.89E+02	2.25E+03
20	1.33E-03	9.99E+02	2.51E+03

Table B. 4 (Cont'd)

20	1.52E-03	1.11E+03	2.76E+03
20	1.71E-03	1.21E+03	3.01E+03
20	1.90E-03	1.32E+03	3.26E+03
20	2.85E-03	1.77E+03	4.34E+03
20	3.79E-03	2.19E+03	5.40E+03
20	5.69E-03	3.01E+03	7.32E+03
20	7.59E-03	3.67E+03	9.04E+03
20	9.49E-03	4.34E+03	1.07E+04
20	1.14E-02	5.00E+03	1.23E+04
20	1.33E-02	5.60E+03	1.38E+04
20	1.52E-02	6.18E+03	1.52E+04
20	1.71E-02	6.75E+03	1.66E+04
20	1.90E-02	7.27E+03	1.79E+04
20	2.85E-02	9.77E+03	2.42E+04
20	3.79E-02	1.22E+04	2.98E+04
35	2.32E-05	1.29E+01	9.22E+01
35	3.09E-05	1.81E+01	1.20E+02
35	3.86E-05	2.37E+01	1.48E+02
35	4.64E-05	3.01E+01	1.74E+02
35	5.41E-05	3.73E+01	1.99E+02
35	6.18E-05	4.40E+01	2.24E+02
35	6.96E-05	5.12E+01	2.48E+02
35	7.73E-05	5.86E+01	2.71E+02
35	1.16E-04	9.03E+01	3.79E+02
35	1.55E-04	1.28E+02	4.81E+02
35	2.32E-04	1.96E+02	6.65E+02
35	3.09E-04	2.58E+02	8.35E+02
35	3.86E-04	3.25E+02	9.88E+02

Table B. 4 (Cont'd)

35	4.64E-04	3.88E+02	1.14E+03
35	5.41E-04	4.43E+02	1.28E+03
35	6.18E-04	5.02E+02	1.42E+03
35	6.96E-04	5.59E+02	1.55E+03
35	7.73E-04	6.09E+02	1.68E+03
35	1.16E-03	8.52E+02	2.27E+03
35	1.55E-03	1.09E+03	2.81E+03
40	5.88E-06	2.27E+00	2.61E+01
40	8.82E-06	3.70E+00	3.85E+01
40	1.18E-05	5.24E+00	5.05E+01
40	1.47E-05	7.11E+00	6.24E+01
40	1.76E-05	9.15E+00	7.38E+01
40	2.06E-05	1.12E+01	8.50E+01
40	2.35E-05	1.34E+01	9.62E+01
40	2.65E-05	1.56E+01	1.07E+02
40	2.94E-05	1.78E+01	1.17E+02
40	4.41E-05	2.90E+01	1.68E+02
40	5.88E-05	4.22E+01	2.17E+02
40	8.82E-05	6.82E+01	3.07E+02
40	1.18E-04	9.49E+01	3.91E+02
40	1.47E-04	1.22E+02	4.70E+02
40	1.76E-04	1.48E+02	5.45E+02
40	2.06E-04	1.74E+02	6.16E+02
40	2.35E-04	2.00E+02	6.84E+02
40	2.65E-04	2.26E+02	7.52E+02
40	2.94E-04	2.51E+02	8.16E+02
40	4.41E-04	3.67E+02	1.12E+03
40	5.88E-04	4.80E+02	1.38E+03

Table B. 4 (Cont'd)

50	5.23E-07	1.51E-01	2.54E+00
50	7.84E-07	2.40E-01	3.71E+00
50	1.05E-06	3.18E-01	4.87E+00
50	1.57E-06	4.47E-01	7.21E+00
50	2.09E-06	6.05E-01	9.55E+00
50	2.61E-06	7.84E-01	1.18E+01
50	3.14E-06	9.96E-01	1.41E+01
50	3.66E-06	1.17E+00	1.64E+01
50	4.18E-06	1.37E+00	1.86E+01
50	4.70E-06	1.63E+00	2.08E+01
50	5.23E-06	1.78E+00	2.30E+01
50	7.84E-06	3.01E+00	3.37E+01
50	1.05E-05	4.42E+00	4.45E+01
50	1.57E-05	7.45E+00	6.49E+01
50	2.09E-05	1.09E+01	8.47E+01
50	2.61E-05	1.46E+01	1.04E+02
50	3.14E-05	1.83E+01	1.22E+02
50	3.66E-05	2.21E+01	1.40E+02
50	4.18E-05	2.62E+01	1.58E+02
50	4.70E-05	2.98E+01	1.75E+02
50	5.23E-05	3.45E+01	1.93E+02
50	7.84E-05	5.57E+01	2.74E+02
50	1.05E-04	7.83E+01	3.49E+02
60	1.97E-07	3.42E-02	9.48E-01
60	2.63E-07	4.77E-02	1.26E+00
60	3.29E-07	6.40E-02	1.56E+00
60	3.95E-07	8.45E-02	1.87E+00
60	4.60E-07	1.03E-01	2.17E+00

Table B. 4 (Cont'd)

60	5.26E-07	1.25E-01	2.46E+00
60	2.63E-06	7.47E-01	1.17E+01
60	3.29E-06	1.00E+00	1.45E+01
60	3.95E-06	1.28E+00	1.73E+01
60	4.60E-06	1.56E+00	2.00E+01
60	5.26E-06	1.82E+00	2.28E+01
60	6.58E-06	2.49E+00	2.81E+01
60	9.87E-06	4.19E+00	4.11E+01
60	1.32E-05	6.02E+00	5.37E+01

Table B. 5 Dynamic Measurement Data for Binder Modified with 5% Linear SBS, (Kraton D1102)

Temperature [°C]	Frequency [rad/s]	G' [Pa]	G'' [Pa]
5	1.26E-01	1.24E+05	2.02E+05
5	1.89E-01	1.61E+05	2.59E+05
5	2.51E-01	1.95E+05	3.14E+05
5	3.14E-01	2.30E+05	3.63E+05
5	3.77E-01	2.64E+05	3.99E+05
5	4.40E-01	2.86E+05	4.36E+05
5	5.03E-01	3.17E+05	4.69E+05
5	5.65E-01	3.36E+05	5.01E+05
5	6.28E-01	3.65E+05	5.34E+05
5	9.42E-01	4.47E+05	6.62E+05
5	1.26E+00	5.36E+05	7.76E+05
5	1.89E+00	7.00E+05	9.70E+05
5	2.51E+00	8.12E+05	1.11E+06
5	3.14E+00	9.36E+05	1.25E+06
5	3.77E+00	1.03E+06	1.37E+06
5	4.40E+00	1.13E+06	1.48E+06
5	5.03E+00	1.21E+06	1.61E+06
5	5.65E+00	1.32E+06	1.69E+06
5	6.28E+00	1.39E+06	1.81E+06
5	9.42E+00	1.83E+06	2.26E+06
5	1.26E+01	2.16E+06	2.63E+06
10	2.37E-02	4.53E+04	7.87E+04
10	3.16E-02	5.06E+04	8.81E+04
10	4.74E-02	6.63E+04	1.16E+05
10	6.31E-02	8.21E+04	1.41E+05

Table B. 5 (Cont'd)

10	7.89E-02	9.63E+04	1.60E+05
10	9.47E-02	1.07E+05	1.80E+05
10	1.10E-01	1.21E+05	1.98E+05
10	1.26E-01	1.33E+05	2.15E+05
10	1.42E-01	1.44E+05	2.32E+05
10	1.58E-01	1.53E+05	2.46E+05
10	2.37E-01	1.92E+05	3.15E+05
10	3.16E-01	2.35E+05	3.73E+05
10	4.74E-01	3.11E+05	4.69E+05
10	6.31E-01	3.65E+05	5.49E+05
10	7.89E-01	4.23E+05	6.22E+05
10	9.47E-01	4.64E+05	6.93E+05
10	1.10E+00	5.11E+05	7.52E+05
10	1.26E+00	5.50E+05	7.98E+05
10	1.42E+00	5.97E+05	8.52E+05
10	1.58E+00	6.24E+05	8.92E+05
10	2.37E+00	7.79E+05	1.10E+06
10	3.16E+00	9.37E+05	1.28E+06
15	1.32E-02	2.80E+04	4.92E+04
15	1.65E-02	3.23E+04	5.77E+04
15	1.98E-02	3.72E+04	6.57E+04
15	2.31E-02	4.12E+04	7.18E+04
15	2.64E-02	4.58E+04	7.87E+04
15	2.97E-02	4.94E+04	8.49E+04
15	3.30E-02	5.26E+04	9.08E+04
15	4.95E-02	6.92E+04	1.20E+05
15	6.59E-02	8.45E+04	1.43E+05
15	9.89E-02	1.07E+05	1.84E+05

Table B. 5 (Cont'd)

15	1.32E-01	1.32E+05	2.21E+05
15	1.65E-01	1.52E+05	2.51E+05
15	1.98E-01	1.75E+05	2.80E+05
15	2.31E-01	1.92E+05	3.05E+05
15	2.64E-01	2.10E+05	3.31E+05
15	2.97E-01	2.26E+05	3.54E+05
15	3.30E-01	2.40E+05	3.75E+05
15	4.95E-01	3.08E+05	4.71E+05
15	6.59E-01	3.61E+05	5.53E+05
30	2.44E-04	1.17E+03	3.05E+03
30	3.67E-04	1.68E+03	4.25E+03
30	4.89E-04	2.16E+03	5.30E+03
30	7.33E-04	3.03E+03	7.15E+03
30	9.78E-04	3.93E+03	8.85E+03
30	1.22E-03	4.80E+03	1.03E+04
30	1.47E-03	5.54E+03	1.16E+04
30	1.71E-03	6.36E+03	1.30E+04
30	1.96E-03	7.03E+03	1.42E+04
30	2.20E-03	7.64E+03	1.54E+04
30	2.44E-03	8.27E+03	1.66E+04
30	3.67E-03	1.13E+04	2.17E+04
30	4.89E-03	1.38E+04	2.63E+04
30	7.33E-03	1.83E+04	3.51E+04
30	9.78E-03	2.28E+04	4.24E+04
30	1.22E-02	2.64E+04	4.92E+04
30	1.47E-02	3.04E+04	5.53E+04
30	1.71E-02	3.38E+04	6.12E+04
30	1.96E-02	3.74E+04	6.70E+04

Table B. 5 (Cont'd)

30	2.20E-02	4.06E+04	7.25E+04
30	2.44E-02	4.28E+04	7.85E+04
30	3.67E-02	5.77E+04	1.04E+05
30	4.89E-02	6.99E+04	1.25E+05
40	3.58E-05	2.11E+02	7.10E+02
40	4.78E-05	2.74E+02	8.99E+02
40	7.17E-05	3.94E+02	1.24E+03
40	9.55E-05	5.27E+02	1.57E+03
40	1.19E-04	6.35E+02	1.86E+03
40	1.43E-04	7.59E+02	2.14E+03
40	1.67E-04	8.64E+02	2.41E+03
40	1.91E-04	9.84E+02	2.67E+03
40	2.15E-04	1.10E+03	2.92E+03
40	2.39E-04	1.21E+03	3.16E+03
40	3.58E-04	1.68E+03	4.29E+03
40	4.78E-04	2.18E+03	5.28E+03
40	7.17E-04	3.06E+03	7.01E+03
40	9.55E-04	3.86E+03	8.62E+03
40	1.19E-03	4.65E+03	1.00E+04
40	1.43E-03	5.38E+03	1.15E+04
40	1.67E-03	6.08E+03	1.28E+04
40	1.91E-03	6.80E+03	1.40E+04
40	2.15E-03	7.37E+03	1.52E+04
40	2.39E-03	7.99E+03	1.63E+04
40	3.58E-03	1.08E+04	2.16E+04
40	4.78E-03	1.33E+04	2.61E+04
50	6.15E-06	3.82E+01	1.59E+02
50	9.23E-06	5.47E+01	2.24E+02

Table B. 5 (Cont'd)

50	1.23E-05	7.31E+01	2.88E+02
50	1.54E-05	9.05E+01	3.48E+02
50	1.85E-05	1.07E+02	4.04E+02
50	2.15E-05	1.22E+02	4.58E+02
50	2.46E-05	1.38E+02	5.12E+02
50	2.77E-05	1.57E+02	5.65E+02
50	3.08E-05	1.74E+02	6.15E+02
50	4.62E-05	2.48E+02	8.58E+02
50	6.15E-05	3.27E+02	1.08E+03
50	9.23E-05	4.91E+02	1.49E+03
50	1.23E-04	6.34E+02	1.86E+03
50	1.54E-04	7.93E+02	2.21E+03
50	1.85E-04	9.27E+02	2.55E+03
50	2.15E-04	1.06E+03	2.86E+03
50	2.46E-04	1.20E+03	3.16E+03
50	2.77E-04	1.32E+03	3.46E+03
50	3.08E-04	1.46E+03	3.72E+03
50	4.62E-04	2.06E+03	5.03E+03
50	6.15E-04	2.61E+03	6.17E+03
60	6.99E-07	3.52E+00	2.45E+01
60	9.31E-07	5.22E+00	3.15E+01
60	1.40E-06	8.30E+00	4.49E+01
60	1.86E-06	1.12E+01	5.77E+01
60	2.33E-06	1.38E+01	7.00E+01
60	2.79E-06	1.66E+01	8.19E+01
60	3.26E-06	1.93E+01	9.37E+01
60	3.73E-06	2.24E+01	1.05E+02
60	4.19E-06	2.45E+01	1.16E+02

Table B. 5 (Cont'd)

60	4.66E-06	2.75E+01	1.28E+02
60	6.99E-06	4.17E+01	1.81E+02
60	9.31E-06	5.66E+01	2.31E+02
60	1.40E-05	8.24E+01	3.24E+02
60	1.86E-05	1.08E+02	4.12E+02
60	2.33E-05	1.36E+02	4.96E+02
60	2.79E-05	1.61E+02	5.77E+02
60	3.26E-05	1.86E+02	6.52E+02
60	3.73E-05	2.11E+02	7.27E+02
60	4.19E-05	2.34E+02	8.00E+02
60	4.66E-05	2.62E+02	8.69E+02
60	6.99E-05	3.84E+02	1.20E+03
60	9.31E-05	4.95E+02	1.51E+03
70	2.23E-08	2.32E-02	9.19E-01
70	3.35E-08	4.24E-02	1.36E+00
70	4.47E-08	6.40E-02	1.81E+00
70	5.59E-08	9.45E-02	2.24E+00
70	6.70E-08	1.20E-01	2.67E+00
70	7.82E-08	1.50E-01	3.10E+00
70	1.01E-07	2.10E-01	3.96E+00
70	1.68E-07	4.64E-01	6.52E+00
70	2.23E-07	7.24E-01	8.60E+00
70	3.35E-07	1.30E+00	1.25E+01
70	4.47E-07	1.91E+00	1.64E+01
70	5.59E-07	2.58E+00	2.01E+01
70	6.70E-07	3.27E+00	2.37E+01
70	7.82E-07	3.95E+00	2.72E+01
70	8.94E-07	4.72E+00	3.07E+01

Table B. 5 (Cont'd)

70	1.01E-06	5.41E+00	3.41E+01
70	1.12E-06	6.15E+00	3.75E+01
70	1.68E-06	9.89E+00	5.33E+01
70	2.23E-06	1.37E+01	6.81E+01

Table B.6 Dynamic Measurement Data for Binder Modified with 3% SIS, (Kraton D1107)

Temperature [°C]	Frequency [rad/s]	G' [Pa]	G'' [Pa]
60	3.66E-06	6.29E+00	7.98E+01
60	4.18E-06	6.76E+00	9.11E+01
60	4.70E-06	7.85E+00	1.02E+02
60	5.23E-06	8.45E+00	1.13E+02
60	7.84E-06	1.17E+01	1.67E+02
60	1.05E-05	1.59E+01	2.20E+02
60	1.57E-05	2.49E+01	3.25E+02
60	2.09E-05	3.60E+01	4.26E+02
60	2.61E-05	4.52E+01	5.27E+02
60	3.14E-05	5.85E+01	6.25E+02
60	3.66E-05	7.04E+01	7.22E+02
60	4.18E-05	8.33E+01	8.18E+02
60	4.70E-05	9.31E+01	9.14E+02
60	5.23E-05	1.06E+02	1.01E+03
50	7.17E-05	1.72E+02	1.24E+03
60	7.84E-05	1.78E+02	1.46E+03
50	9.55E-05	2.41E+02	1.60E+03
60	1.05E-04	2.46E+02	1.90E+03
50	1.19E-04	3.12E+02	1.95E+03
50	1.43E-04	3.91E+02	2.29E+03
50	1.67E-04	4.56E+02	2.62E+03
50	1.91E-04	5.30E+02	2.95E+03
50	2.15E-04	5.91E+02	3.27E+03
50	2.39E-04	6.75E+02	3.59E+03
50	3.58E-04	1.04E+03	5.10E+03

Table B. 6 (Cont'd)

30	3.98E-04	1.24E+03	5.02E+03
50	4.78E-04	1.41E+03	6.51E+03
30	4.98E-04	1.57E+03	6.04E+03
40	5.25E-04	1.62E+03	6.68E+03
30	5.97E-04	1.89E+03	7.02E+03
40	6.56E-04	2.04E+03	8.03E+03
30	6.97E-04	2.20E+03	7.96E+03
40	7.88E-04	2.42E+03	9.32E+03
30	7.97E-04	2.51E+03	8.85E+03
30	8.96E-04	2.80E+03	9.74E+03
40	9.19E-04	2.80E+03	1.06E+04
30	9.96E-04	3.08E+03	1.06E+04
40	1.05E-03	3.20E+03	1.18E+04
40	1.18E-03	3.59E+03	1.30E+04
20	1.28E-03	3.92E+03	1.33E+04
40	1.31E-03	3.94E+03	1.41E+04
30	1.49E-03	4.65E+03	1.47E+04
20	1.92E-03	6.14E+03	1.79E+04
40	1.97E-03	5.90E+03	1.95E+04
30	1.99E-03	5.94E+03	1.85E+04
20	2.56E-03	7.88E+03	2.25E+04
40	2.62E-03	7.69E+03	2.46E+04
30	2.99E-03	8.65E+03	2.53E+04
20	3.85E-03	1.13E+04	3.07E+04
30	3.98E-03	1.11E+04	3.14E+04
30	4.98E-03	1.36E+04	3.76E+04
20	5.13E-03	1.47E+04	3.82E+04
30	5.97E-03	1.60E+04	4.28E+04

Table B. 6 (Cont'd)

20	6.41E-03	1.80E+04	4.49E+04
30	6.97E-03	1.83E+04	4.81E+04
20	7.70E-03	2.03E+04	5.16E+04
30	7.97E-03	2.06E+04	5.32E+04
30	8.96E-03	2.30E+04	5.81E+04
20	8.98E-03	2.32E+04	5.78E+04
30	9.96E-03	2.51E+04	6.31E+04
20	1.03E-02	2.62E+04	6.38E+04
20	1.15E-02	2.90E+04	6.93E+04
20	1.28E-02	3.14E+04	7.46E+04
30	1.49E-02	3.52E+04	8.47E+04
20	1.92E-02	4.33E+04	9.99E+04
30	1.99E-02	4.52E+04	1.05E+05
10	2.48E-02	5.42E+04	1.17E+05
20	2.56E-02	5.48E+04	1.22E+05
10	3.30E-02	6.72E+04	1.44E+05
20	3.85E-02	7.52E+04	1.62E+05
10	4.96E-02	9.22E+04	1.91E+05
20	5.13E-02	9.54E+04	1.99E+05
5	6.28E-02	1.08E+05	2.23E+05
20	6.41E-02	1.13E+05	2.32E+05
10	6.61E-02	1.16E+05	2.33E+05
20	7.70E-02	1.27E+05	2.63E+05
10	8.26E-02	1.40E+05	2.69E+05
20	8.98E-02	1.43E+05	2.92E+05
5	9.42E-02	1.42E+05	2.84E+05
10	9.91E-02	1.58E+05	3.02E+05
20	1.03E-01	1.58E+05	3.20E+05

Table B. 6 (Cont'd)

20	1.15E-01	1.73E+05	3.46E+05
10	1.16E-01	1.76E+05	3.38E+05
5	1.26E-01	1.80E+05	3.46E+05
20	1.28E-01	1.86E+05	3.70E+05
10	1.32E-01	1.95E+05	3.68E+05
10	1.49E-01	2.14E+05	3.96E+05
10	1.65E-01	2.29E+05	4.22E+05
5	1.89E-01	2.49E+05	4.50E+05
20	1.92E-01	2.49E+05	4.82E+05
10	2.48E-01	3.04E+05	5.48E+05
5	2.51E-01	3.08E+05	5.37E+05
20	2.56E-01	3.06E+05	5.77E+05
5	3.14E-01	3.54E+05	6.18E+05
10	3.30E-01	3.74E+05	6.50E+05
5	3.77E-01	4.06E+05	7.05E+05
5	4.40E-01	4.52E+05	7.69E+05
10	4.96E-01	4.92E+05	8.35E+05
5	5.03E-01	4.96E+05	8.26E+05
5	5.65E-01	5.32E+05	8.95E+05
5	6.28E-01	5.73E+05	9.52E+05
10	6.61E-01	6.10E+05	9.90E+05
10	8.26E-01	7.03E+05	1.13E+06
5	9.42E-01	7.66E+05	1.18E+06
10	9.91E-01	7.78E+05	1.26E+06
10	1.16E+00	8.59E+05	1.37E+06
5	1.26E+00	9.21E+05	1.42E+06
10	1.32E+00	9.35E+05	1.48E+06
10	1.49E+00	1.01E+06	1.58E+06

Table B. 6 (Cont'd)

10	1.65E+00	1.08E+06	1.68E+06
5	1.89E+00	1.20E+06	1.80E+06
10	2.48E+00	1.44E+06	2.12E+06
5	2.51E+00	1.44E+06	2.10E+06
5	3.14E+00	1.70E+06	2.40E+06
10	3.30E+00	1.76E+06	2.50E+06
5	3.77E+00	1.92E+06	2.62E+06
5	4.40E+00	2.14E+06	2.88E+06
5	5.03E+00	2.35E+06	3.10E+06
5	5.65E+00	2.56E+06	3.30E+06
5	6.28E+00	2.74E+06	3.51E+06
5	9.42E+00	3.54E+06	4.34E+06
5	1.26E+01	4.24E+06	5.00E+06

Table B. 7 Dynamic Measurement of Data for Binder Modified with 5% SIS, (Kraton D1107)

Temperature [°C]	Frequency [rad/s]	G' [Pa]	G'' [Pa]
5	9.42E-02	1.32E+05	2.00E+05
5	1.26E-01	1.61E+05	2.41E+05
5	1.89E-01	2.08E+05	3.02E+05
5	2.51E-01	2.51E+05	3.48E+05
5	3.14E-01	2.83E+05	3.85E+05
5	3.77E-01	3.09E+05	4.24E+05
5	4.40E-01	3.39E+05	4.63E+05
5	5.03E-01	3.68E+05	4.89E+05
5	5.65E-01	3.87E+05	5.19E+05
5	6.28E-01	4.14E+05	5.49E+05
5	9.42E-01	5.17E+05	6.47E+05
5	1.26E+00	6.06E+05	7.58E+05
5	1.88E+00	7.52E+05	9.04E+05
5	2.51E+00	8.49E+05	1.05E+06
5	3.14E+00	9.50E+05	1.15E+06
5	3.77E+00	1.05E+06	1.25E+06
5	4.40E+00	1.13E+06	1.33E+06
5	5.03E+00	1.20E+06	1.40E+06
5	5.65E+00	1.27E+06	1.48E+06
5	6.28E+00	1.33E+06	1.56E+06
5	9.42E+00	1.69E+06	1.90E+06
5	1.26E+01	1.99E+06	2.17E+06
10	2.59E-02	5.84E+04	9.64E+04
10	3.47E-02	7.14E+04	1.16E+05
10	5.21E-02	9.41E+04	1.49E+05

Table B. 7 (Cont'd)

10	6.91E-02	1.15E+05	1.74E+05
10	8.65E-02	1.30E+05	1.95E+05
10	1.04E-01	1.44E+05	2.18E+05
10	1.21E-01	1.60E+05	2.39E+05
10	1.39E-01	1.74E+05	2.53E+05
10	1.56E-01	1.84E+05	2.73E+05
10	1.73E-01	1.97E+05	2.89E+05
10	2.59E-01	2.58E+05	3.53E+05
10	3.47E-01	3.02E+05	4.17E+05
10	5.18E-01	3.83E+05	5.10E+05
10	6.91E-01	4.38E+05	5.82E+05
10	8.65E-01	4.96E+05	6.52E+05
10	1.04E+00	5.56E+05	7.12E+05
10	1.21E+00	5.95E+05	7.68E+05
10	1.39E+00	6.38E+05	8.08E+05
10	1.56E+00	6.81E+05	8.60E+05
10	1.73E+00	7.10E+05	8.97E+05
10	2.59E+00	8.68E+05	1.08E+06
10	3.47E+00	1.01E+06	1.23E+06
20	1.14E-03	6.58E+03	1.36E+04
20	1.71E-03	9.05E+03	1.68E+04
20	2.29E-03	1.10E+04	2.06E+04
20	3.44E-03	1.48E+04	2.72E+04
20	4.57E-03	1.84E+04	3.29E+04
20	5.71E-03	2.15E+04	3.78E+04
20	6.86E-03	2.41E+04	4.25E+04
20	8.01E-03	2.68E+04	4.75E+04
20	9.15E-03	2.96E+04	5.15E+04

Table B. 7 (Cont'd)

20	1.03E-02	3.20E+04	5.55E+04
20	1.14E-02	3.42E+04	5.93E+04
20	1.71E-02	4.53E+04	7.70E+04
20	2.29E-02	5.46E+04	9.12E+04
20	3.42E-02	7.17E+04	1.17E+05
20	4.57E-02	8.84E+04	1.38E+05
20	5.71E-02	1.01E+05	1.58E+05
20	6.86E-02	1.14E+05	1.77E+05
20	8.01E-02	1.25E+05	1.92E+05
20	9.15E-02	1.37E+05	2.07E+05
20	1.03E-01	1.47E+05	2.22E+05
20	1.14E-01	1.57E+05	2.34E+05
20	1.71E-01	1.98E+05	2.91E+05
20	2.29E-01	2.35E+05	3.39E+05
30	1.88E-04	1.65E+03	3.61E+03
30	2.51E-04	2.08E+03	4.39E+03
30	3.77E-04	2.82E+03	5.87E+03
30	5.01E-04	3.56E+03	7.20E+03
30	6.27E-04	4.21E+03	8.37E+03
30	7.52E-04	4.72E+03	9.51E+03
30	8.78E-04	5.29E+03	1.07E+04
30	1.00E-03	5.89E+03	1.17E+04
30	1.13E-03	6.38E+03	1.27E+04
30	1.25E-03	6.87E+03	1.36E+04
30	1.88E-03	9.29E+03	1.81E+04
30	2.51E-03	1.14E+04	2.19E+04
30	3.75E-03	1.54E+04	2.88E+04
30	5.01E-03	1.94E+04	3.49E+04

Table B. 7 (Cont'd)

30	6.27E-03	2.29E+04	4.04E+04
30	7.52E-03	2.57E+04	4.57E+04
30	8.78E-03	2.88E+04	5.07E+04
30	1.00E-02	3.19E+04	5.50E+04
30	1.13E-02	3.48E+04	5.94E+04
30	1.25E-02	3.74E+04	6.36E+04
40	4.21E-06	6.99E+01	2.20E+02
40	5.63E-06	9.06E+01	2.72E+02
40	8.44E-06	1.31E+02	3.69E+02
40	1.12E-05	1.67E+02	4.60E+02
40	1.40E-05	2.00E+02	5.52E+02
40	1.68E-05	2.35E+02	6.29E+02
40	1.97E-05	2.68E+02	7.02E+02
40	2.25E-05	2.98E+02	7.76E+02
40	2.52E-05	3.25E+02	8.47E+02
40	2.81E-05	3.54E+02	9.21E+02
40	4.21E-05	5.02E+02	1.24E+03
40	5.63E-05	6.23E+02	1.54E+03
40	8.40E-05	8.71E+02	2.08E+03
40	1.12E-04	1.08E+03	2.56E+03
40	1.40E-04	1.31E+03	3.04E+03
40	1.68E-04	1.51E+03	3.45E+03
40	1.97E-04	1.70E+03	3.87E+03
40	2.25E-04	1.89E+03	4.25E+03
40	2.52E-04	2.07E+03	4.63E+03
40	2.81E-04	2.27E+03	4.99E+03
40	4.21E-04	3.13E+03	6.64E+03
40	5.63E-04	3.96E+03	8.09E+03

Table B.7 (Cont'd)

50	1.48E-07	2.38E+00	1.41E+01
50	2.22E-07	3.91E+00	2.00E+01
50	2.95E-07	5.50E+00	2.56E+01
50	3.69E-07	7.07E+00	3.08E+01
50	4.43E-07	8.59E+00	3.57E+01
50	5.17E-07	1.00E+01	4.06E+01
50	5.91E-07	1.16E+01	4.53E+01
50	6.64E-07	1.28E+01	4.99E+01
50	7.38E-07	1.43E+01	5.44E+01
50	1.11E-06	2.12E+01	7.53E+01
50	1.48E-06	2.75E+01	9.51E+01
50	2.21E-06	3.93E+01	1.32E+02
50	2.95E-06	5.02E+01	1.65E+02
50	3.69E-06	6.14E+01	1.99E+02
50	4.43E-06	7.27E+01	2.29E+02
50	5.17E-06	8.26E+01	2.58E+02
50	5.91E-06	9.25E+01	2.87E+02
50	6.64E-06	1.02E+02	3.15E+02
50	7.38E-06	1.12E+02	3.42E+02
50	1.11E-05	1.61E+02	4.70E+02
50	1.48E-05	2.06E+02	5.85E+02
60	5.68E-09	3.11E-02	6.82E-01
60	7.59E-09	4.63E-02	9.04E-01
60	1.14E-08	7.62E-02	1.34E+00
60	1.51E-08	1.14E-01	1.77E+00
60	1.89E-08	1.58E-01	2.20E+00
60	2.27E-08	2.06E-01	2.61E+00
60	2.65E-08	2.51E-01	3.03E+00

Table B. 7 (Cont'd)

60	3.03E-08	3.13E-01	3.45E+00
60	3.40E-08	3.79E-01	3.85E+00
60	3.78E-08	4.35E-01	4.25E+00
60	5.68E-08	7.52E-01	6.21E+00
60	7.59E-08	1.11E+00	8.00E+00
60	1.13E-07	1.85E+00	1.16E+01
60	1.51E-07	2.55E+00	1.49E+01
60	1.89E-07	3.37E+00	1.79E+01
60	2.27E-07	4.11E+00	2.10E+01
60	2.65E-07	4.91E+00	2.39E+01

Table B. 8 Dynamic Measurement Data for Binder Modified with 3% EVA, (Elvax 350)

Temperature [°C]	Frequency [rad/s]	G' [Pa]	G'' [Pa]
5	6.28E-02	9.19E+04	1.81E+05
5	9.42E-02	1.17E+05	2.30E+05
5	1.26E-01	1.45E+05	2.78E+05
5	1.89E-01	1.99E+05	3.65E+05
5	2.51E-01	2.44E+05	4.39E+05
5	3.14E-01	2.81E+05	5.10E+05
5	3.77E-01	3.22E+05	5.86E+05
5	4.40E-01	3.60E+05	6.42E+05
5	5.03E-01	3.98E+05	6.95E+05
5	5.65E-01	4.26E+05	7.60E+05
5	6.28E-01	4.62E+05	8.11E+05
5	9.42E-01	6.14E+05	1.03E+06
5	1.26E+00	7.54E+05	1.24E+06
5	1.89E+00	9.95E+05	1.62E+06
5	2.51E+00	1.20E+06	1.91E+06
5	3.14E+00	1.39E+06	2.18E+06
5	3.77E+00	1.61E+06	2.42E+06
5	4.40E+00	1.78E+06	2.67E+06
5	5.03E+00	1.94E+06	2.90E+06
5	5.65E+00	2.11E+06	3.08E+06
5	6.28E+00	2.26E+06	3.29E+06
5	9.42E+00	3.01E+06	4.16E+06
5	1.26E+01	3.63E+06	4.87E+06
10	1.33E-02	2.75E+04	6.03E+04
10	1.77E-02	3.40E+04	7.43E+04

Table B. 8 (Cont'd)

10	2.66E-02	4.65E+04	9.92E+04
10	3.55E-02	5.86E+04	1.21E+05
10	4.44E-02	6.99E+04	1.41E+05
10	5.32E-02	7.89E+04	1.59E+05
10	6.21E-02	8.84E+04	1.79E+05
10	7.10E-02	9.81E+04	1.96E+05
10	7.99E-02	1.07E+05	2.11E+05
10	8.87E-02	1.15E+05	2.26E+05
10	1.33E-01	1.54E+05	2.98E+05
10	1.77E-01	1.89E+05	3.57E+05
10	2.66E-01	2.53E+05	4.69E+05
10	3.55E-01	3.15E+05	5.62E+05
10	4.44E-01	3.67E+05	6.47E+05
10	5.32E-01	4.15E+05	7.32E+05
10	6.21E-01	4.59E+05	8.06E+05
10	7.10E-01	5.04E+05	8.78E+05
10	7.99E-01	5.45E+05	9.40E+05
10	8.87E-01	5.86E+05	1.00E+06
10	1.33E+00	7.79E+05	1.29E+06
10	1.77E+00	9.59E+05	1.54E+06
20	1.65E-04	6.59E+02	2.28E+03
20	2.48E-04	9.57E+02	3.17E+03
20	3.30E-04	1.26E+03	3.98E+03
20	4.96E-04	1.87E+03	5.46E+03
20	6.61E-04	2.40E+03	6.78E+03
20	8.26E-04	2.84E+03	8.12E+03
20	9.91E-04	3.36E+03	9.32E+03
20	1.16E-03	3.87E+03	1.05E+04

Table B. 8 (Cont'd)

20	1.32E-03	4.36E+03	1.15E+04
20	1.49E-03	4.79E+03	1.26E+04
20	1.65E-03	5.20E+03	1.36E+04
20	2.48E-03	7.45E+03	1.85E+04
20	3.30E-03	9.24E+03	2.28E+04
20	4.96E-03	1.29E+04	3.06E+04
20	6.61E-03	1.63E+04	3.74E+04
20	8.26E-03	1.93E+04	4.39E+04
20	9.91E-03	2.24E+04	5.03E+04
20	1.16E-02	2.51E+04	5.62E+04
20	1.32E-02	2.79E+04	6.17E+04
20	1.49E-02	3.04E+04	6.70E+04
20	1.65E-02	3.29E+04	7.23E+04
20	2.48E-02	4.48E+04	9.57E+04
20	3.30E-02	5.49E+04	1.17E+05
30	8.40E-06	2.30E+01	1.72E+02
30	1.12E-05	3.23E+01	2.23E+02
30	1.68E-05	5.19E+01	3.21E+02
30	2.24E-05	7.28E+01	4.16E+02
30	2.80E-05	9.31E+01	5.06E+02
30	3.36E-05	1.14E+02	5.94E+02
30	3.92E-05	1.36E+02	6.79E+02
30	4.48E-05	1.61E+02	7.63E+02
30	5.04E-05	1.85E+02	8.42E+02
30	5.60E-05	2.05E+02	9.19E+02
30	8.40E-05	3.16E+02	1.29E+03
30	1.12E-04	4.16E+02	1.64E+03
30	1.68E-04	6.50E+02	2.27E+03

Table B. 8 (Cont'd)

30	2.24E-04	8.58E+02	2.87E+03
30	2.80E-04	1.06E+03	3.43E+03
30	3.36E-04	1.27E+03	3.96E+03
30	3.92E-04	1.46E+03	4.46E+03
30	4.48E-04	1.66E+03	4.96E+03
30	5.04E-04	1.86E+03	5.43E+03
30	5.60E-04	2.04E+03	5.89E+03
40	5.17E-06	1.32E+01	1.15E+02
40	5.91E-06	1.55E+01	1.29E+02
40	6.64E-06	1.80E+01	1.44E+02
40	7.38E-06	1.99E+01	1.59E+02
40	1.11E-05	3.31E+01	2.30E+02
40	1.48E-05	4.55E+01	2.97E+02
40	2.22E-05	7.40E+01	4.24E+02
40	2.95E-05	1.03E+02	5.46E+02
40	3.69E-05	1.32E+02	6.62E+02
40	4.43E-05	1.58E+02	7.76E+02
40	5.17E-05	1.85E+02	8.84E+02
40	5.91E-05	2.16E+02	9.91E+02
40	6.64E-05	2.46E+02	1.09E+03
40	7.38E-05	2.71E+02	1.20E+03
40	1.11E-04	4.21E+02	1.67E+03
40	1.48E-04	5.63E+02	2.12E+03
50	3.93E-07	8.71E-01	9.77E+00
50	5.24E-07	1.17E+00	1.29E+01
50	7.86E-07	1.80E+00	1.90E+01
50	1.05E-06	2.40E+00	2.50E+01
50	1.31E-06	3.01E+00	3.08E+01

Table B. 8 (Cont'd)

50	1.57E-06	3.57E+00	3.66E+01
50	1.83E-06	4.14E+00	4.25E+01
50	2.10E-06	4.99E+00	4.82E+01
50	2.36E-06	5.79E+00	5.39E+01
50	2.62E-06	6.39E+00	5.93E+01
50	3.93E-06	9.82E+00	8.68E+01
50	5.24E-06	1.41E+01	1.13E+02
50	7.86E-06	2.18E+01	1.64E+02
50	1.05E-05	3.08E+01	2.13E+02
50	1.31E-05	3.95E+01	2.60E+02
50	1.57E-05	4.94E+01	3.05E+02
50	1.83E-05	5.86E+01	3.50E+02
50	2.10E-05	6.82E+01	3.94E+02
50	2.36E-05	7.66E+01	4.37E+02
50	2.62E-05	8.68E+01	4.79E+02
50	3.93E-05	1.34E+02	6.82E+02
50	5.24E-05	1.82E+02	8.70E+02
60	2.62E-07	6.32E-01	6.72E+00
60	3.93E-07	8.90E-01	9.89E+00
60	5.24E-07	1.12E+00	1.30E+01
60	7.86E-07	1.70E+00	1.91E+01
60	1.05E-06	2.26E+00	2.51E+01
60	1.31E-06	2.81E+00	3.10E+01
60	1.57E-06	3.37E+00	3.69E+01
60	1.83E-06	3.97E+00	4.25E+01
60	2.10E-06	4.68E+00	4.82E+01
60	2.36E-06	5.26E+00	5.37E+01
60	2.62E-06	6.05E+00	5.93E+01

Table B. 8 (Cont'd)

60	3.93E-06	9.60E+00	8.65E+01
60	5.24E-06	1.31E+01	1.13E+02

Table B. 9 Dynamic Measurement Data for Binder Modified with 5% EVA, (Elvax 350)

Temperature [°C]	Frequency [rad/s]	G' [Pa]	G'' [Pa]
5	6.28E-02	1.85E+04	3.30E+04
5	9.42E-02	2.33E+04	4.15E+04
5	1.26E-01	2.84E+04	5.09E+04
5	1.89E-01	3.76E+04	6.60E+04
5	2.51E-01	4.58E+04	7.96E+04
5	3.14E-01	5.32E+04	9.11E+04
5	3.77E-01	6.12E+04	1.02E+05
5	4.40E-01	6.72E+04	1.12E+05
5	5.03E-01	7.32E+04	1.22E+05
5	5.65E-01	7.92E+04	1.31E+05
5	6.28E-01	8.50E+04	1.42E+05
5	9.42E-01	1.08E+05	1.77E+05
5	1.26E+00	1.31E+05	2.08E+05
5	1.89E+00	1.66E+05	2.58E+05
5	2.51E+00	2.03E+05	3.08E+05
5	3.14E+00	2.23E+05	3.39E+05
5	3.77E+00	2.51E+05	3.74E+05
5	4.40E+00	2.69E+05	4.02E+05
5	5.03E+00	2.92E+05	4.36E+05
5	5.65E+00	3.11E+05	4.69E+05
5	6.28E+00	3.28E+05	4.93E+05
5	9.42E+00	4.05E+05	6.18E+05
5	1.26E+01	4.68E+05	7.26E+05
10	3.76E-01	6.04E+04	1.01E+05
10	5.01E-01	7.14E+04	1.19E+05

Table B. 9 (Cont'd)

10	6.27E-01	8.39E+04	1.39E+05
10	7.52E-01	9.64E+04	1.58E+05
20	3.15E-03	2.80E+03	6.47E+03
20	4.72E-03	3.42E+03	7.03E+03
20	6.30E-03	4.20E+03	8.46E+03
20	9.45E-03	5.66E+03	1.10E+04
20	1.26E-02	7.03E+03	1.31E+04
20	1.57E-02	8.16E+03	1.49E+04
20	1.89E-02	9.05E+03	1.67E+04
20	2.20E-02	1.02E+04	1.86E+04
20	2.52E-02	1.12E+04	2.00E+04
20	2.83E-02	1.19E+04	2.15E+04
20	3.15E-02	1.28E+04	2.30E+04
20	4.72E-02	1.72E+04	2.96E+04
20	6.30E-02	2.03E+04	3.55E+04
20	9.45E-02	2.66E+04	4.58E+04
20	1.26E-01	3.16E+04	5.40E+04
20	1.57E-01	3.63E+04	6.21E+04
20	1.89E-01	4.09E+04	6.93E+04
20	2.20E-01	4.48E+04	7.55E+04
20	2.52E-01	4.86E+04	8.23E+04
20	2.83E-01	5.13E+04	8.72E+04
20	3.15E-01	5.48E+04	9.24E+04
20	4.72E-01	6.81E+04	1.15E+05
20	6.30E-01	7.79E+04	1.31E+05
30	2.65E-04	3.02E+02	8.70E+02
30	3.03E-04	3.43E+02	9.67E+02
30	3.41E-04	3.78E+02	1.06E+03

Table B. 9 (Cont'd)

30	3.79E-04	4.16E+02	1.15E+03
30	5.68E-04	5.86E+02	1.57E+03
30	7.57E-04	7.45E+02	1.94E+03
30	1.14E-03	1.05E+03	2.64E+03
30	1.51E-03	1.36E+03	3.25E+03
30	1.89E-03	1.64E+03	3.83E+03
30	2.27E-03	1.89E+03	4.40E+03
30	2.65E-03	2.13E+03	4.91E+03
30	3.03E-03	2.39E+03	5.38E+03
30	3.41E-03	2.63E+03	5.87E+03
30	3.79E-03	2.86E+03	6.32E+03
30	5.68E-03	4.01E+03	8.37E+03
30	7.57E-03	5.03E+03	1.02E+04
40	4.89E-05	6.37E+01	2.26E+02
40	7.33E-05	9.13E+01	3.16E+02
40	9.78E-05	1.20E+02	3.96E+02
40	1.22E-04	1.46E+02	4.76E+02
40	1.47E-04	1.75E+02	5.49E+02
40	1.71E-04	1.99E+02	6.21E+02
40	1.96E-04	2.24E+02	6.88E+02
40	2.20E-04	2.49E+02	7.54E+02
40	2.44E-04	2.74E+02	8.20E+02
40	3.67E-04	3.95E+02	1.12E+03
40	4.89E-04	5.08E+02	1.40E+03
50	1.27E-06	2.86E+00	1.03E+01
50	1.69E-06	3.61E+00	1.31E+01
50	2.54E-06	4.99E+00	1.83E+01
50	3.39E-06	6.05E+00	2.36E+01

Table B. 9 (Cont'd)

50	4.24E-06	7.30E+00	2.85E+01
50	5.08E-06	8.49E+00	3.34E+01
50	5.93E-06	9.73E+00	3.80E+01
50	6.78E-06	1.09E+01	4.25E+01
50	7.63E-06	1.19E+01	4.69E+01
50	8.47E-06	1.29E+01	5.14E+01
50	1.27E-05	1.87E+01	7.23E+01
50	1.69E-05	2.37E+01	9.27E+01
50	2.54E-05	3.38E+01	1.29E+02
50	3.39E-05	4.41E+01	1.65E+02
50	4.24E-05	5.43E+01	1.98E+02
50	5.08E-05	6.41E+01	2.29E+02
50	5.93E-05	7.46E+01	2.60E+02
50	6.78E-05	8.34E+01	2.90E+02
50	7.63E-05	9.27E+01	3.20E+02
50	8.47E-05	1.02E+02	3.47E+02
50	1.27E-04	1.48E+02	4.81E+02
50	1.69E-04	1.89E+02	6.04E+02

APPENDIX - C

Dynamic Measurement Data for Glass Transition Temperatures

**Table C. 1 Dynamic Measurement Data of Base Asphalt
at Frequency 0.1 Hz**

Temperature [K]	G' [Pa]	G'' [Pa]
233	6.31E+08	50600000
238	5.3E+08	72300000
243	3.61E+08	92100000
253	91500000	47100000
263	5300000	8200000
273	540000	1200000
283	40000	140000
293	3600	17000
298	630	8300
303	370	3000
313	34	540
323	11	160
333	1.2	62

Table C. 2 Dynamic Measurement Data of Binder Modified with 5% Radial SBS, (Finaprene) at Frequency 0.1 Hz

Temperature [K]	G' [Pa]	G'' [Pa]
243	3230000	694000
253	1770000	1870000
263	1080000	1240000
273	812000	981000
283	531000	654000
293	90300	137000
303	20900	29500
313	6350	8910
323	1560	3100
333	467	1180

**Table C. 3 Dynamic Measurement Data of Binder Modified with
5% Linear SBS, (Kraton D1102) at Frequency 0.1 Hz**

Temperature [K]	G' [Pa]	G'' [Pa]
233	4.8E+08	48000000
238	3.8E+08	57000000
243	2.7E+08	59000000
253	1E+08	42000000
263	23000000	16000000
268	6060000	5250000
273	2730000	3180000
278	1220000	1590000
283	515000	737000
293	82400	140000
303	8700	18000
313	1500	4400
323	460	1600
333	60	410

Table C. 4 Dynamic Measurement Data of Binder Modified with 5% EVA, (Elvax 350) at Frequency 0.1 Hz

Temperature [K]	G' [Pa]	G'' [Pa]
243	3.3E+08	95000000
253	80000000	48000000
263	11000000	11000000
273	1600000	2100000
283	330000	480000
293	47000	83000
303	3800	9800
313	670	2000
323	120	570
333	18	160

**Table C. 5 Dynamic Measurement Data of Base Asphalt
at Frequency 1 Hz**

Temperature [K]	G' [Pa]	G'' [Pa]
233	6.96E+08	13600000
238	6.19E+08	34300000
243	4.82E+08	65200000
253	1.89E+08	67800000
263	15000000	19000000
273	2600000	4600000
283	310000	780000
293	32000	110000
298	11000	47000
303	5000	24000
313	680	5200
323	100	1300
333	23	370

Table C. 6 Dynamic Measurement Data of Binder Modified with 5% Radial SBS, (Finaprene 411) at Frequency 1 Hz

Temperature [K]	G' [Pa]	G'' [Pa]
243	58000000	24000000
253	50000000	28000000
263	1.55E+07	10804000
273	2.68E+06	2396000
283	905000	894000
293	413000	527000
303	86700	131000
313	24900	35800
323	8930	12300
333	2960	5180

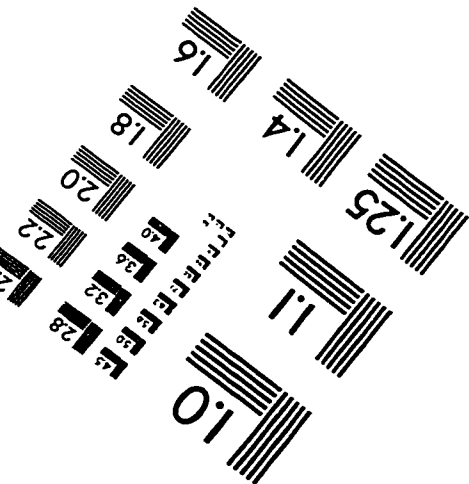
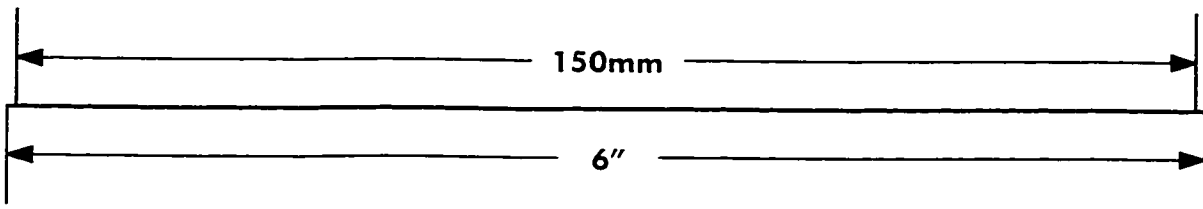
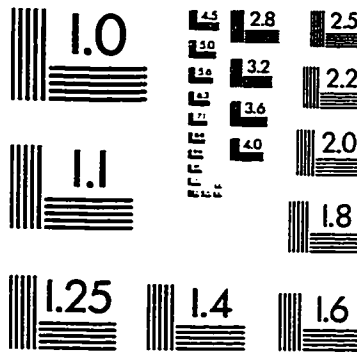
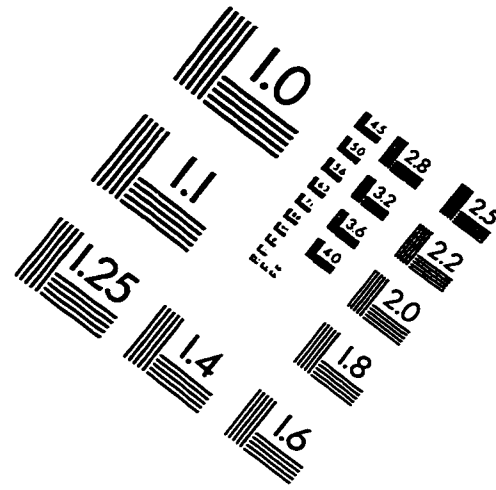
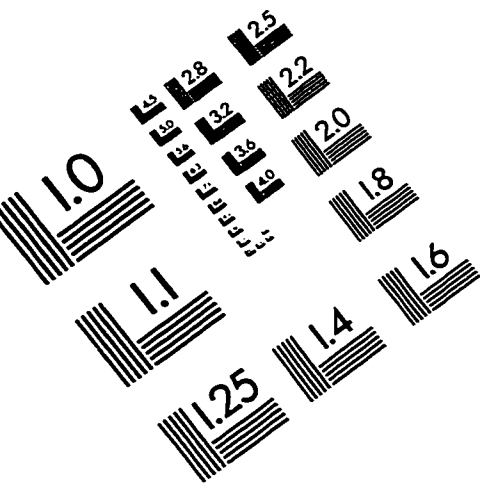
Table C. 7 Dynamic Measurement Data of Binder Modified with 5% Linear SBS, (Kraton D1102) at Frequency 1 Hz

Temperature [K]	G' [Pa]	G'' [Pa]
233	5.5E+08	31000000
238	4.6E+08	43000000
243	3.6E+08	52000000
253	1.7E+08	50000000
263	53000000	27000000
268	16900000	11400000
273	6050000	6860000
278	3130000	4180000
283	1620000	2080000
293	357000	545000
303	45000	91000
313	15000	23000
323	4200	9400
333	940	3000

Table C. 8 Dynamic Measurement Data of Binder Modified with 5% EVA, (Elvax 350) at Frequency 1 Hz

Temperature [K]	G' [Pa]	G'' [Pa]
243	4.7E+08	78000000
253	1.7E+08	69000000
263	36000000	27000000
273	6700000	7200000
283	1400000	1800000
293	240000	370000
303	26000	53000
313	5800	15000
323	1100	3900
333	260	1400

IMAGE EVALUATION TEST TARGET (QA-3)



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