

**CHARACTERIZATION OF AGED
POLYMER MODIFIED ASPHALT CEMENTS
FOR RECYCLING PURPOSES**

A Dissertation

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GLOSSARY OF TERMS

Asphalt cement:	Asphalt cement is a dark brown to black cementitious material that is either naturally occurring or is produced by petroleum distillation ¹ .
Tar:	Tar is primarily manufactured from the destructive distillation of bituminous coal and has a very distinct odor ¹ .
Aggregate:	A mixture of sand, gravel, and crushed stone
Shoving:	Deformations of the pavement surface, most common in intersections, where there is braking and stopping traffic. It is easiest to detect at intersections where transverse striping becomes "wavy".
Rutting:	Permanent deformations of the pavement (indentations) in the wheel paths; most common in intersections, where there is braking and stopping traffic.
Asphalt Binder:	Asphalt cement
Mix:	It refers to a mixture of asphalt cement (binder) and aggregate.
Fatigue (alligator) Cracking:	Interconnected cracking with a pattern resembling alligator skin. Pavement that is fatigued or "worn out" from heavy traffic.
Stripping:	The liquid asphalt binder holds the pavement together and waterproofs the pavement. When moisture gets to the surface of the aggregate it can break the asphalt – aggregate bond, causing the pavement to disintegrate.

PMAC:	Polymer Modified Asphalt Cement.
RAP:	Reclaimed (Recycled) Asphalt Pavement
HMA:	Hot Mix Asphalt.
Asphaltenes:	One of the principal components of asphalt. It is the black or brown solid material precipitated from an asphalt with normal pentane. It is an arbitrary fraction defined by the method of analysis. Other arbitrary fractions of asphalt are oils and resins. ²
Maltenes:	Maltenes constitute the fraction of asphalt which is soluble in n-alkane solvent such as pentane and heptane. ³
SHRP:	Strategic Highway Research Program
LMS:	Low Molecular weight Species
DOT:	Department of Transportation
SBS:	Styrene-Butadiene-Styrene tri-block copolymer
SBR:	Styrene-Butadiene Rubber statistical copolymer

ABSTRACT

Since polymer modified asphalt cement (PMAC) has been employed for a decade, the lifetime and wear on some of these pavements is reaching a stage where resurfacing is necessary. This research focuses on the characterization of aged polymer modified asphalt cements (PMAC) to evaluate their potential for recycling. A styrene-butadiene-styrene tri-block (SBS) polymer modified asphalt cement was selected and characterized using standard asphalt binder qualification techniques, i.e., the Superpave PG protocol.

We developed a procedure to characterize the relative concentration of polymer in asphalt cements by gel permeation chromatography (GPC). Infrared spectrographic, thermogravimetric and rheological techniques were used to identify changes in the binder components as a result of aging. The impact of the extraction and recovery process on binder properties has been ascertained and found to be minimal. Two field aged polymer modified asphalt cements were extracted from field-aged asphalt cores. An eight year old field aged polymer modified asphalt binder was recovered from a wearing course mixture located on US61 Hwy in Livingston Parish, Louisiana. Samples of three, five and seven year old field aged PMAC binders was recovered from a wearing course mixture located on Interstate I55 near Granada, Mississippi. A correlation between field aging time and simulated aging by PAV was developed; PAV with humidity proved to be the best prediction. A comparison was established between the field aged materials and a series of lab aged binders. All binders were characterized with respect to their composition and rheological properties. In general, residual polymer was detected using gel permeation chromatography analysis except when extensive oxidative age hardening of the binder had occurred. Samples from the surface of US61 were

quite brittle at low temperature, as demonstrated by forced ductility tests. Core samples of the same asphalt binder were more tractable, thus less aged, but recycling of this material will require additives to restore the desired rheological properties to the binder blend.

CHAPTER 1 INTRODUCTION

Overview

There are two main types of road pavements, rigid road pavement, and flexible road pavement. The rigid type is represented by concrete cement pavements for which Portland cement comprises the binder. The flexible type of pavements, known as hot mix asphalt (HMA) pavement, will be the focus of this work.

The HMA pavements are complex engineered materials comprised of multiple layers, each one with its own properties and function within the final pavement structure. There should be at least four layers to all asphalt cement pavements (figure 1-1):

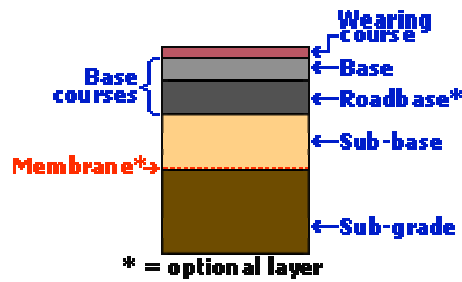


Figure 1-1.
Asphalt cement pavement typical layers.

The sub-base and base course layers may be constructed from more than one individual layer of the specified material, but for our purposes, we will consider each layer as being a single entity. Sometimes, levels permitting, an existing asphalt cement or concrete surface can be overlaid with a new wearing course. This is acceptable provided that the new surfacing is properly bonded to the old surface.⁴

The focus of this research is on the wearing course, the very top part of the pavement where oxidation and aging due to oxidation occurs mostly. More specific than that, the scope of this research is to characterize the binder properties, binder which typically represents 5% by weight of the wearing course. Even though the properties and characteristics of this layer have an important influence over the service life and the overall performance of the pavement as a whole, it still represents just a fraction of the whole structure. Its properties and performance are an integrant part of a larger structure, thus having only a partial influence over the overall properties and service life of a pavement.

Background

Asphalt cement for paving applications has been used for centuries. However, the asphalt intrinsic properties, such as the low temperature cracking, fatigue cracking and the permanent deformation at high temperature, as well as its age hardening, are limiting factors for utilization of unmodified asphalt cement (AC) on highly demanding routes of today.⁵ Therefore modification of asphalts using polymers has increased steadily within the last several years because it improves many desired properties that have resulted in enhanced contribution of asphalt binders to build pavements having better performances.⁶⁻⁹ In many states, including Louisiana, polymer modified asphalt cements (PMAC's) have been specified for all new road construction. The wearing characteristics of PMAC's have been excellent, but many of the initial PMAC placements are reaching the end of their lifetimes and resurfacing must be scheduled.

Recycling of asphalt pavements (RAP) is not new to the highway industry. As early as in the 1930s, there were reports on the use of RAP.¹⁰ It was not, however, until the mid to late

1970s, that hot mix asphalt recycling became popular.¹¹ Today with the increase of construction price (raw materials like asphalt and aggregates) and especially the awareness for environmental protection, the use of recycled pavements has become more and more important. Sources suggest that every year more than 45 million tons of HMA are being removed from deteriorating pavements in the United States.¹² Reconstructing the pavements requires about the same amount of raw materials. If we simply choose to dispose of the waste HMA, large quantities of raw aggregates need to be transported from various sources and more and more land fills need to be built to accommodate the wastes. Using the recycled asphalt pavements makes use of materials, which otherwise, must be hauled to a landfill, reduces the demand for new sources of material (quarries and asphalt binder), and, in many cases, can reduce construction cost. It is both beneficial in reducing the cost of highway construction and environmental protection. Therefore, some states even have imposed rules that require certain percentage of waste pavements be recycled. Currently in Louisiana, 100 percent of reclaimed asphalt pavement materials are being recycled into highway usage in one form or another. Although recycled asphalt pavements (RAP) can be used for various purposes such as granular shoulders, embankments or any form of filling materials, the most preferred usage is as asphalt bound layer somewhere in the pavement structure. Depending on which layer of the asphalt pavement is being reconstructed using RAP, the maximum percentage of recycled material included in the new mix ranges from 25% for wearing courses up to 98% for the base layers.

Recycling of Polymer Modified Asphalt Cement Pavement

The Louisiana Department of Transportation and Development (LADOTD) has adopted the use of polymer modified asphalt cement (PMAC) in most of its hot mix asphalt mixtures since 1994. Little research has been conducted on recycling of polymer modified asphalt pavements

because there was not an urgent need for this topic. But as more and more PMAC pavements are being constructed, this problem has become more and more relevant. The earliest PMAC pavements built in Louisiana were in late 1980s. They have already approached the time for rehabilitation. In order to fully utilize the potential of waste material, it is necessary to evaluate the fundamental characteristics of recycled polymer modified asphalt pavements and develop a practical procedure on how to design and construct flexible pavements using recycled polymer modified asphalt pavements.

Addition of appropriate polymers to asphalt binders can significantly improve the performance of asphalt concrete pavements, e.g. increasing fatigue cracking resistance, reducing the extent of permanent deformation, improving thermal cracking resistance, minimizing moisture sensitivity and potentially reducing age hardening.^{13, 14} The positive contribution of polymer additives to asphalt binder performance has prompted a number of state transportation departments to require that polymer be incorporated into all asphalt pavements. The predominant polymers incorporated in the PMAC are elastomers such as styrene-butadiene rubber (SBR)^{15, 16} or styrene-butadiene-styrene (SBS) block copolymers.¹⁷

The extensive use of polymer modified asphalt cements improves asphalt pavement performance. However, several critical questions associated with recycling of polymer modified asphalt cements remain to be answered. It has been reported that some additives in asphalt mixtures caused difficulties during recycling. For example, latex rubber modified asphalt mixes tend to gum up the teeth on the milling machine. Sulfur enriched asphalt mixes release toxic fumes during the process of re-heating.¹⁸ Clearly, before recycling of polymer modified asphalt mixtures, certain technical questions need to be answered before it can be accepted by the industry. These questions can be summarized as follows:

- Will the polymer additives degrade or harden during long term exposure to field conditions and thus no longer contribute to the binder properties?
- What fundamental material characteristics will the binder and mixes have at different percentages of recycled polymer modified asphalt mixes?
- How can the binder consistency be adjusted in recycled-virgin asphalt blends to restore the properties of PMAC's?

The role played by time and environmental factors on aging of asphalt cements within the pavement applications is a subject of continuous interest.¹⁹⁻²⁹ Earlier studies carried out on the effect of temperature and relative humidity on the oxidation of airblown asphalts as a function of exposure time showed that the rate of oxidation is dependent on both of these environmental factors.¹⁹⁻²¹ The behavior of bitumens was studied in hot mix wearing courses subjected to climates ranging from hot and dry summers to continental cold winter with much heavier rainfall.^{20, 21} The environmental temperature effect on the age hardening characteristics of asphalt binders is rather well documented.

Hardening is due to chemical reactions, including oxidation, polymerization, and condensation and/or due to physical processes, including loss of volatiles and structural morphological change. However, reaction with oxygen has been shown to be the principal factor responsible for hardening of asphalt in the road.^{22-24, 27, 29} It has been concluded that the high average air temperature (thermal oxidation) is the most significant factor affecting the rate and amount of asphalt hardening in hot climates.^{22, 25, 26}

To mimic road aging of asphalt pavements, testing at increased temperature has been widely used, since the rate of most oxidation reactions approximately doubles for each 10°C increase.²² Diffusion of oxygen has been shown to control aging.^{23, 28} Therefore, aging was

considered as a chemical as well as a physical problem.²³ Voids and aggregate porosity were also found to be contributing factors but were dependent upon the type of asphalt and average temperature.²⁴ Laboratory protocols were recently developed under the Strategic Highway Research Program (SHRP) to simulate the field hardening of asphalt binder and mixes in which the mean annual air temperatures prevalent during field aging have been taken into account. The influence of atmospheric humidity has not been considered.³⁰ Dynamic Shear Rheometry (DSR) testing conducted both on laboratory aged and field aged binders, was used to correlate changes in physical properties upon aging. However, only a recommended provisional protocol applicable for non-modified binder was presented.

The climate of continental United States is diverse. Most of US Southeast states experience both hot and wet summer weather. While the July mean temperature and mean precipitation for Louisiana and Mississippi are the same (32.2/34.4°C and 1,220-1,625 mm), some states might experience a higher temperature (e.g., 37.8°C for Texas and Oklahoma) or more rain (e.g., 1,980-2,030 mm for Carolinas).³¹ Extremely high relative humidity and a low dew point maintain more often than not a continuous film of water on the Gulf Coast roads during the night and early morning hours. One might wonder therefore if the laboratory protocols for aging asphalt binders should not consider also the vapors of water as components of the aging atmosphere.

Aging in presence of water of several SHRP core asphalts and of two polymer modified asphalt cements has been investigated recently at Western Research Institute from Laramie, WY.³² Analytical methods have been developed to assess the chemical composition of asphalts before and after aging. However, while very interesting data have been reported, no real connection has been made with data on similar asphalts extracted from long term aged asphalt

pavements. The aim of this dissertation is to characterize aged polymer modified asphalt cements and assess the potential problems associated with their recycling.

Asphalt Cement

The main source of asphalt for paving applications is crude oil with a high specific gravity. The asphalt properties depend on the source of the crude and the type of refining process used. Asphalt production comes from the residues left after various distillation fractions of the crude oil have been separated and it is not one of the main profit generating processes for the refinery. The residual component suited for asphalt cement (AC) varies from 1 to 85 percent.³³ The properties of the residue are dependent on the conditions under which it was separated; the higher the atmospheric equivalent vapor temperature used (the higher the degree of oxidation sustained by the asphalt cement), the harder the residual asphalt. Accordingly, the grading system used in the United States is based on the viscosity of the original asphalt, specifying the properties of the mixtures. Grading requirements for asphalt cement viscosity are specified in the American Society for Testing Materials (ASTM) D 3381. For example, AC-10 is an asphalt cement with a viscosity of 1000 poise at 60 °C (140°F), which is “softer” than AC-30, an asphalt cement with a viscosity of 3000 poise at 60 °C.

The chemical characteristics and properties of the asphalt are very diverse due to a wide variety of originating sources. As a consequence asphalt cements are not characterized by their chemical composition but by their properties in the total blend of components. Asphalt cements are generally considered to be mixtures of large, complex and often polyfunctional molecules that can be separated into asphaltenes and maltenes. Asphaltenes, which comprise the most complex fraction, are mixtures of paraffin-naphtene-aromatics with polycyclic structures, including sulfur, oxygen, and nitrogen containing heterocyclic compounds with

some complex metals e.g. nickel and vanadium.³⁴ Maltenes, the hydrocarbon soluble components, contain both neutral oils and aromatic resins. The resins disperse the asphaltenes throughout the oils, making asphalt analogous to a colloidal system.³⁵ Durable asphalts are comprised of these components interacting to form a balanced, compatible system.

Polymer Modified Asphalt Cements

The application of asphalt is limited due to its intrinsic properties. The inherent weaknesses of the asphalt make the maintenance of the highway system quite difficult and expensive. Asphalt can be shear sensitive making it prone to shove and rut at higher temperatures. On the other hand, at low temperatures it becomes brittle and tends to undergo fracture cracking and potholing. Permanent deformation, fatigue cracking, and low temperature cracking are generally considered to be the most significant manifestations of distresses in asphalt-surfaced pavements.³⁶ Cracking is generally reduced by making the asphalt cement either less viscous or less temperature susceptible. Reducing low temperature viscosity leads to soft asphalt and the mechanical properties of mixture deteriorate. Polymer additives provide more flexibility at low temperatures and higher rigidity at higher temperatures since these mixes are less temperature susceptible. In fact the use of asphalt/polymer blends has been progressing rapidly from the experimental stage into mainstream use as the improved physico-mechanical properties of polymer/asphalt cements are demonstrated.^{37, 38}

Since the advent of paving blocks in 1824, efforts to improve the properties of asphalt surfacing materials have centered on polymeric additives. In the 1840's patents describing the modification of bitumen with gutta percha or natural rubber appeared, and as each new polymer was developed, its potential interaction with asphalt was evaluated. A successful modification of an asphalt binder with a polymer should improve one or more of the basic asphalt properties

such as rigidity, elasticity, brittleness, durability, and compatibility, especially in-blend compatibility. An asphalt-polymer blend is considered compatible if the polymer is soluble in the asphalt cement or if it can be swollen by the asphalt oils without causing flocculation of the asphaltenes.^{39, 40}

Polymers typically used in polymer modified asphalt cements (PMAC) include plastomers, elastomers, and fibers. Examples are natural rubber latexes, synthetic rubber latexes (SBR), block copolymers of styrene with butadiene or isoprene, polyethylene, polypropylene and other polyolefins, and ethylene-vinyl acetate copolymers.^{8, 37, 41-44}

Basic Principles of Viscoelasticity

Extensive research has been done over the last decade in studying the rheology of asphalt and asphalt concrete.⁷ The implementation of the performance-related specifications for asphalt cements⁴⁵ developed by the Strategic Highway Research Program, SHRP, in which the rheological characterization plays an important role, gave a strong impetus for a thorough investigation of rheological behavior of asphalt binders.^{8, 46, 47} Dynamic shear tests are advantageous because the data can be acquired within the linear range of the asphalt in a loading mode that is similar to that of traffic loading. These measurements are particularly useful in the transition region where delayed elasticity is a major portion of the material response.⁴⁶

In dynamic mechanical analysis, DMA, a sinusoidal strain or stress is applied to a sample and the response is monitored as a function of frequency.⁴⁸ The shear stress σ and the deformation (strain) γ are related via the shear modulus G as follows:

$$\sigma = G \gamma \quad (\text{eq 1})$$

The shear modulus is often known as the rigidity. The reciprocal is the shear compliance, J . Generally the measurements are represented as a complex modulus G^* (vide *infra*) to insure an accurate expression:

$$G^* = G' + iG'' \quad (\text{eq. 2})$$

where: $i^2 = -1$

If stress $\sigma(t)$ is applied, then altered with time t and angular frequency ω according to:

$$\sigma(t) = \sigma_0 \sin \omega t \quad (\text{eq. 3})$$

where σ_0 is the amplitude, an ideal energy elastic body deformation instantly follows the applied stress, and consequently,

$$\gamma(t) = \gamma_0 \sin \omega t \quad (\text{eq. 4})$$

Neither polymers nor asphalt cements are ideal energy elastic bodies; they are viscoelastic materials. In such cases the deformation (strain) lags behind the applied stress (Figure 1-2). With ideal viscoelastic bodies, the resulting phase angle δ in the corresponding vector diagram can be assumed constant, such that the deformation or the strain is

$$\gamma(t) = \gamma_0 \sin (\omega t - \delta) \quad (\text{eq. 5}).$$

The stress vector can be similarly considered to be the sum of two components. One component, $\sigma' = \sigma_0 \cos \delta$, is in phase with the deformation, the other component, on the other hand, $\sigma'' = \sigma_0 \sin \delta$, is not. A modulus can be assigned to each of these two components. The real modulus, or storage modulus, G' , measures the rigidity and resistance to deformation of the sample. It is related to the complex modulus of rigidity G^* by

$$G' = \sigma' / \gamma_0 = (\sigma_0 / \gamma_0) \cos \delta = G^* \cos \delta \quad (\text{eq. 6})$$

The imaginary, or loss modulus, G'' , on the other hand, reflects the loss of useful mechanical energy through dissipation as heat. Similarly, G'' is given by

$$G'' = \sigma'' / \gamma_0 = G^* \sin \delta \quad (\text{eq. 7})$$

Introducing the complex variables, one may rewrite eqs. 3 and 4 as follows:

$$\sigma^* = \sigma_0 e(i\omega t) \quad (\text{eq. 8})$$

and
$$\gamma^* = \gamma_0 e(i\omega t - \delta) \quad (\text{eq. 9})$$

The complex modulus G^* may be then expressed as shown in eq. 2.

Instead of following the deformation (strain) produced by a given stress, the sample can be strained and the resulting stress can be measured. The complex compliance $J^* = 1/G^*$ is obtained in this case, and the storage and loss compliance are correspondingly given by

$$G' = J' / [(J')^2 + (J'')^2] \quad (\text{eq. 10})$$

$$G'' = J'' / [(J')^2 + (J'')^2] \quad (\text{eq. 11})$$

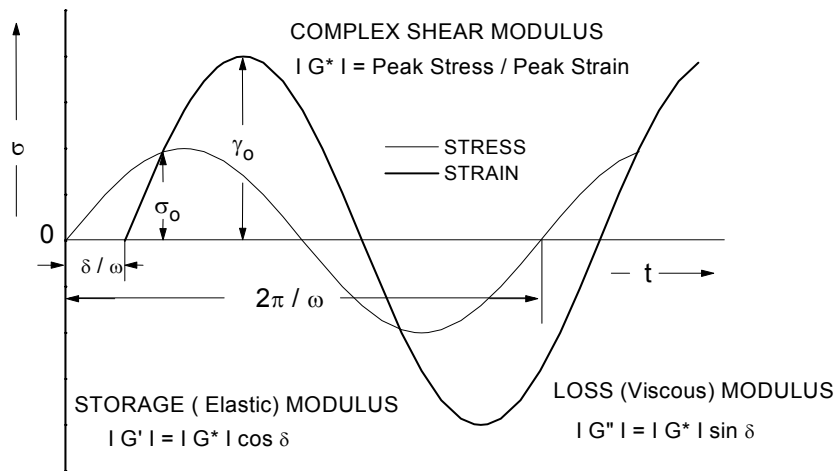


Figure 1-2.
 Schematic representation of the stress σ as a function of time t with dynamic (sinusoidal) loading (strain).

In a stress controlled instrument (both the Bohlin CS rheometer and the Seiko DMS110 module are stress controlled instruments) force is transmitted in accordance to the generated sine wave to the specimen, through the probe, by means of the function generator. The strain produced in the sample is detected by a differential transformer and produces a signal that expresses the dynamic viscoelasticity of the sample from the force (stress) and the strain. This is termed stress controlled testing, in contrast to the strain controlled DMA, in which a sinusoidal varying stress is applied and the strain response is measured. The Bohlin VOR rheometer controls the strain or strain rate while the stress is measured.

Although extensive data can be acquired using dynamic mechanical analysis, selection of the correct parameters in the data analysis for predicting service performance of asphalt binders is not immediately obvious. The primary response of interest is the complex dynamic shear modulus at frequency ω , $G^*(\omega)$ expressed in Pa. As already shown, this modulus is given by the ratio between the absolute magnitude of the dynamic shear stress, $\tau(\omega)$, Pa, and the absolute magnitude of the applied dynamic shear strain, $\gamma(\omega)$, m/m:

$$G^*(\omega) = \frac{|\tau(\omega)|}{|\gamma(\omega)|} \quad (\text{eq. 12})$$

In reporting the results of DMA testing, use is often made of the two other parameters derived above, i.e. the storage and the loss moduli, $G'(\omega)$ and $G''(\omega)$, respectively, and the loss tangent, or tangent of the phase angle, δ , which indicates the lag in the response compared to the applied strain or stress. For purely elastic materials, the phase angle will be zero, whereas for purely viscous materials, the phase angle will be 90° . Thus, the phase angle, expressed as its *sine* or *tangent*, is an important parameter for describing the viscoelastic properties of a paving material. The loss tangent is calculated simply as the tangent of the phase angle, or alternatively, as the ratio of the loss to storage moduli.

The various relationships described above, i.e., the complex, storage and loss moduli, and the phase angle are illustrated by the trigonometry of a right triangle, as shown schematically in Figure 1-3. It follows that the loss tangent can be calculated simply as the tangent of the phase angle, or alternatively, as the ratio of the loss to storage moduli:

$$\tan \delta = G'' / G' \quad (\text{eq. 13})$$

and that

$$G^* = [(G')^2 + (G'')^2]^{1/2} \quad (\text{eq. 14})$$

In analyzing the asphalt cements and the related materials, G^* , the ratio of the peak stress to the peak strain, reflects the total stiffness. The in-phase component of $|G^*|$, i.e. the shear *storage modulus*, G' , represents the part of the input energy which is not lost to heat (the elastic portion). The out-of-phase component of $|G^*|$, i.e. the shear *loss modulus* G'' , represents viscous component of it. The complex dynamic shear viscosity η^* can be obtained from G^* divided by the frequency, while the dynamic viscosity is $\eta = G'' / \omega$. Therefore at temperatures at least 20°C above the T_g , any of these three parameters should relate to flow under load. In the present study G'' was selected as the parameter to evaluate the viscous flow of asphalt binders under investigation.

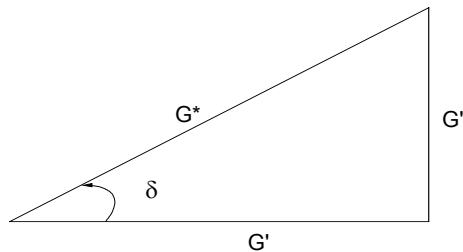


Figure 1-3. Relationships among dynamic moduli and the phase angle shown schematically through the trigonometry of a right triangle.

In a master representation of DMA data, based on the principle of time(frequency)-temperature superposition, a viscoelastic function is plotted against frequency (temperature) through the agency of the William-Landel-Ferry equation (WLF)⁴⁹:

$$\log(aT)/(aT_d) = -C_1(T-T_d)/(C_2+T-T_d) \quad (\text{eq. 15})$$

where:

aT/aT_d = the shift factor relative to the defining temperature, T_d

C_1 & C_2 = empirically determined constants

T = the selected temperature, in °C or °K, and

T_d = the defining temperature, in °C or °K, which is a characteristic parameter for each asphalt cement. T_d is considered as the threshold temperature to glassy state, i.e. it represents the glass transition or T_g of the respective material. The values of C_1 and C_2 depend on the particular morphology or structure associated with a given sample. The C_1 parameter has the highest effect on the appearance of the master representation. A proper master curve should appear smooth and continuous. For amorphous materials, the best approximations for the parameters are $C_1 = 17$ and $C_2 = 56$.⁴⁹ As the sample becomes more crystalline (e.g. polyethylene or the asphalt paraffins) or crosslinked (such as a vulcanized rubber), the values of C_1 and C_2 will increase, reflecting changes in the free volume and the expansion with respect to temperature. For example, in analyzing the shift factor data for SHRP asphalts, it has been found the best values of C_1 and C_2 for use in WLF equation are 19 and 92, respectively.⁴⁷ For some materials it may not be possible to generate a "perfect" master plot as some of the data points may deviate from the smooth, continuous curve. This may be the case of filled or semicrystalline materials. The semicrystalline materials may undergo some additional crystallization when heated above T_g causing an increase in G' modulus and a decrease in $\tan\delta$.

This causes the data points to shift vertically. Data may also deviate from the smooth master curve if collected at very high frequencies (50 Hz and higher).

The WLF equation as applied to asphalts is primarily intended for use in a rigorous pavement performance model, and in predicting viscoelastic functions at times and temperatures for which measurements have not been made. It has been widely used to predict the temperature shift factors, a_T , for asphalt binders, allowing the generation of all kind of rheological master curves.^{7, 46, 47}

The basis for applying dynamic mechanical testing to asphalt characterization has been thoroughly established. However, it must be recognized that asphalts are complex mixtures and the use of a few simple parameters to evaluate the results may lead to erroneous conclusions. Thus, it is advisable to conduct sufficient testing of each asphalt sample to prepare a master curve and determine the proper shift factors for each type of asphalt. Further, the addition of insoluble rubber additives to asphalt will have a marked influence on the rheology of the blends, but measurements on these blends must be made with care to assure that an accurate assessment of the blend properties is obtained.

CHAPTER 2 METHODS AND MATERIALS

Materials

Asphalt Binder

A standard SBS elastomer polymer modified asphalt cement (PMAC) meeting Louisiana DOTD specification for PG 76-22M was obtained from Koch Materials Company, Wichita, KS. The supplier also provided samples of the AC-30 asphalt and of the polymer additive, Solprene. Tables 1 and 2 present the specification and test results for PAC-40 and PG 70-22M, respectively. The original binder was short- and long-term aged to simulate in-service aging of binders. This binder is referred to thereafter as lab-aged RPMAC. An eight plus years old asphalt binder was extracted from road samples taken from US61 Hwy (Livingston Parish, LA). Initially US61S was designated as field aged PMAC, but subsequent investigations of core samples revealed that they were better representatives of field aged RPMAC. Samples obtained by bump grinding of the ¼ inch surface layer were designated as US61S and those from cores were labeled US61C.

In order to obtain field aged samples with different ages from the same roadway, a test section of I55 in Mississippi near Granada was chosen for study. The binder was a Ergon PG 76-22M, the result of blending 85% wt PG 64-22 with 15% wt PEN 150/SBS solution so that the final polymer concentration in the binder is 2.8% wt. The field aged samples were 3 and 5 year old cores along with a 7 year old loose mix collected by Mississippi DOT. Also virgin binder laboratory made cores were received.

Test Factorials

Superpave physical tests on asphalt binder employing a rotational viscometer, a dynamic shear rheometer and a bending beam rheometer were conducted on virgin and aged PMAC binders used in this study. Chemical analysis methods, such as DSC, FTIR and GPC, were also conducted on virgin and aged PMAC binders to identify the impact of the laboratory extraction methods developed in this study.

Table 2-1: Asphalt cement specifications meeting LADOD PAC-40 HG

SPECIFICATIONS	
Original Properties	
	LADOTD PAC-40HG
Viscosity, 140°F (60°C), Poises	Min. 4000
Viscosity, 275°F (135°C), centistokes	Max. 2000
Penetration, 77°F (2°C), 100 g, 5 s, min.	50 - 75
Flash Point, Cleveland open cup, min. °F (°C)	450 (232)
Solubility in trichloroethylene, min., %	99.0
Separation of Polymer, 325°F (163°C), 48 hrs	
Difference in softening point from top and bottom, max., °C	2.0
Force Ductility Ratio, (F ₂ /F ₁ , 39°F (4°C), 5 cm/min, @ 30 cm elongation, min.) F ₂ = F @ 30 cm, F ₁ = Peak Force	0.3
Test on residue from thin-film oven test	
Viscosity, 140°F (60°C), Poises	-
Ductility, 77°F (25°C), 5 cm/min, min., cm	-
Penetration Retention, min., % of original	50
Elastic Recovery, 25°C @ 10 cm elongation, % min.	60
PROPERTIES	
Original Properties	
Asphalt Cement Source	Koch Materials
Asphalt Cement Grade	PAC - 40HG
Penetration @ 25°C	59
Specific Gravity 25 / 25°C	1.03
Absolute Viscosity @ 60°C, Poises	6629
Properties after R. T. F. O.	
Penetration @ 25°C	38
Absolute Viscosity @ 60°C, Poises	18524

Table 2-2. Asphalt cement specifications meeting Superpave PG 70-22

Test	Property	Test Results	PG Criteria
Original Binder			
Flash Point	N/A	-	230°C
Rotational Viscosity (Pa·s)	135°C @100 rpm	1.125	3 Pa·s, Max
Dynamic Shear Rheometer (kPa)	$G^*/\sin \delta$	@ 70°C 1.782 @ 76°C 1.029	1.0 kPa, Min
TFOT Aged Binder			
Mass Loss (%)	N/A	< 1.0	1% Max.
Dynamic Shear Rheometer (kPa)	$G^*/\sin \delta$	@ 70°C 3.232 @ 76°C 1.772	2.20 kPa, Min
PAV Aged Binder			
Dynamic Shear Rheometer (kPa)	$G^*\sin \delta$	@28°C 1036.3 @ 31°C 707.4	5000 kPa, Max.
Bending Beam Rheometer (-12°C)	Stiffness	110	300 MPa, Max.
Bending Beam Rheometer (-12°C)	M value	0.39	0.300, Min.
PG Grading		70-22	

Materials Characterization

Thermal Analysis

The glass transition and melting transitions of the binders were measured using differential scanning calorimetry (DSC). DSC was performed using a Seiko 220 DSC, a TA Instruments DSC 2920 Modulated DSC, and a Universal V2.6D TA instrument, all calibrated for temperature and enthalpy with indium. A typical DSC measurement was conducted on $\cong 10$ mg sample sealed in an aluminum sample pan using a similar empty pan with cap as a reference. Larger samples, up to 40 mg, were employed to estimate the T_g of the binders.

These samples were heated to 80°C for 30 minutes to eliminate prior thermal history and quenched in liquid nitrogen before mounting in a DSC cell; measurements were initiated at -50°C. Thermogravimetric (TG) analysis was conducted on extracted samples using a TA Instruments Hi-Res Modulated TGA 2950 Thermogravimetric Analyser . The sample for TG analysis (\cong 10 mg) was contained in an open aluminum sample pans using an empty aluminum sample pan as a reference.

FTIR Spectroscopy

The functional group composition of the binders was examined by qualitative Fourier Transform Infrared (FTIR) using a Perkin Elmer 1700 FTIR spectrophotometer. Films of asphalts and rubber were cast from 10%wt solutions in toluene on a NaCl plate and analyzed taking the blank plate as background.

GPC Characterization

The molecular weight distribution of the asphalt components was estimated by using a gel permeation chromatograph equipped with a Waters 590 pump and a Waters model 410 differential refractive index detector. The separation of the polymer from the asphalt components was effected with two Phenogel 10 μ , 300 x 7.8 mm columns (Phenomenex, Torrance, CA), connected in series (1) 10-5 Å (10 K - 1,000 K); (2) MXM (5 K – 500 K). The column set was calibrated with narrow molecular weight polystyrene standards ranging from 1,060 to 523,000 Daltons. All samples were prepared at a concentration of 2%wt in tetrahydrofuran (THF) and 100 μ L samples were injected at room temperature. Samples were eluted with THF at 0.8 mL/min and the polymer concentration in the eluent was recorded using a differential refractometer.

Forced Ductility

This test was conducted as per ASTM P226. A copper mold was coated with release agent (baby oil plus baby powder) and molten asphalt was poured into it to form a dog-bone specimen with a 3 cm test area. The specimen in the mold was placed in a constant temperature bath set at $4 \pm 1^\circ\text{C}$, allowed to equilibrate, and the excess asphalt trimmed from the specimen. The trimmed mold was replaced in the bath, re-equilibrated, and then the specimen was removed. The sample was strained at 5 cm/min up to a maximum extension of 30 cm. The force required to apply the strain is plotted versus time. A normal test produced a chart record showing two peaks. The second peak will be less than the initial peak. The tensile stress ratio is defined as the force (f_2) at the second peak divided by the force of the initial peak (f_1). A sample passes the test if it stretches at least 1000 percent.

Rheological Measurements

A high torque controlled stress AR2000 rheometer specially designed for characterization of soft materials (TA Instruments Inc Waters Corp., New Castle, DE) was used to determine the complex viscoelastic modulus G^* (describing rigidity) of asphalt binders. The geometry included a set of 8 and 25 mm steel parallel plates ($h = 1\text{-}3\text{ mm}$) for the instrument working as a dynamic shearing Rheometer (DSR, Figure 2-1) and asphalt torsion bars (3x6x40 mm) for working as a dynamic mechanical analyzer (DMA, Figure 2-2). An environmental temperature control (ETC) oven allowed a precise control of temperature within 0.1°C (Figures 2-1 and 2-2). While both DSR and DMA modes provided similar results around room temperature 30°C , the torsion bars were used at negative temperatures while the DSR mode (*vide infra*) was preferred at higher temperatures (above 50°C). Test procedures included dynamic temperature

ramp determinations using low heating or cooling rates (0.25 to 1°C/min) and a sweep of frequencies covering two decades (0.5-50 rad/s; 5 points/decade).



Figure 2-1.
Setting of the instrument in DSR mode. ETC open



Figure 2-2.
Setting of the instrument in DMA mode. ETC open

DSR Measurements

A Bohlin CVO dynamic shear rheometer, DSR, specially designed for characterization of asphalt cements (Bohlin Instruments Div., Metric Group Inc., Cranbury, NJ) was used to investigate the rheological behavior of the virgin PMAC and field recovered binder. This test was performed according to AASHTO TP5.⁵⁰ The testing parameters were the following:

measurement type - high temperature range; target temperature - different values; strain amplitude - 12.0 percent; plate diameter - 25.0 mm; plate gap - 1,000 μm (1.0 mm); and equilibration time - 3.0 min

Bending Beam Rheometer Measurements

The bending beam rheometer (Cannon TEBBR) was used to measure the low-temperature creep response of PAV aged binders. This test was performed as per AASHTO TP1.⁵¹ Data was collected at six loading times (8, 15, 30, 60, 120 and 240 sec) for a load on the beam of 100 ± 5 g.

Supercritical Binder Extraction Procedure

Extraction of asphalts from RPMAC should be complete in order to determine its physical properties for recycling purposes. The extraction method should not adversely affect the material, for example by oxidation during the extraction and/or concentration steps.

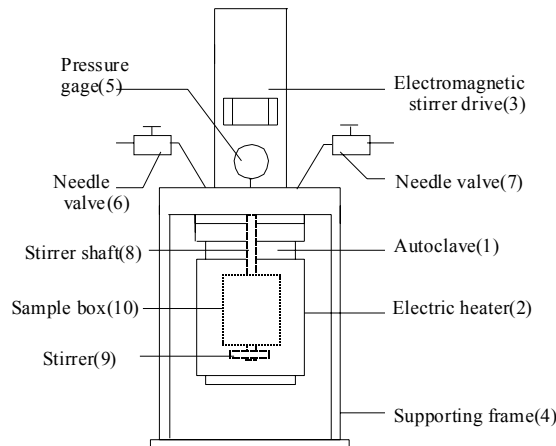


Figure 2-3.
Schematic presentation of the autoclave for SCF extraction.

The sample was extracted with a mixture of toluene (T) and dimethyl ether (DME) at a pressures and temperatures higher than the critical parameters for DME (126.9°C and 53.7 atm,

respectively). In a typical extraction experiment 2g of PMAC were introduced in the sample box 10 (Figure 2-3) made of fine mesh stainless steel sieve and was extracted with a mixture of T (200 g) and DME (50g) for 2 hours at 130-150°C and 700-800 psi (14.21 psi = 1 atm). The pressure was adjusted with argon compressed at 1,600 psi through the needle valve 6.

When the extraction was considered finished, the temperature was allowed to decrease to 20-30 °C and the pressure was dropped to atmospheric conditions ($\cong 1$ atm) by releasing both the argon and DME (DME boils at -15 °C at 1atm) through the needle valve 7. The extract was concentrated in vacuum (100 mm Hg @ 95 °C) using a rotary evaporator. The absence of the solvent in the extracted material was checked by thermogravimetry (*vide infra*) in inert nitrogen atmosphere at 150°C (T boils at 110 °C at 1 atm) using a thermogravimetric (TG) balance.

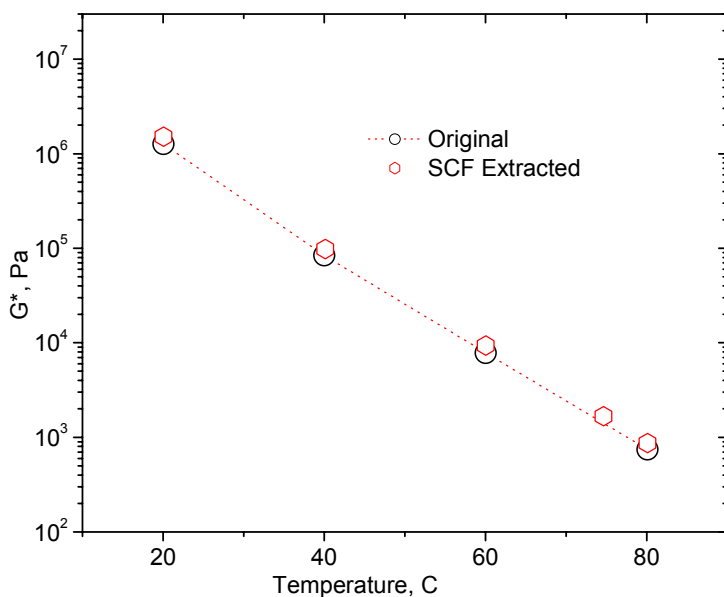


Figure 2-4.
Temperature dependence of the modulus of rigidity of PMAC samples before (Original) and after extraction in supercritical conditions (SCF Extracted).

Furthermore, the rheological properties of the material extracted in SCF conditions were compared to that of the original PMAC in order to determine if the extraction process altered the material properties. As shown in Figure 2-4, the complex modulus of rigidity G^* of the extracted sample compares very well with that of the original PMAC over the whole range of temperatures tested.

Atmospheric Soxhlet Extraction Procedure

Since the SCF extract was completely soluble in toluene, extraction of the binder from the mix was performed also at atmospheric pressure using a Soxhlet apparatus (Figure 2-5) and hot toluene. A nitrogen blanket was applied in order to avoid oxidation. The extract was vacuum-filtered in order to separate the dust carried out by the flowing toluene and concentrated in vacuum (100 mm Hg @ 95 °C) using a rotary evaporator (Figure 2-6). Further the solvent traces were removed in a vacuum oven at 0.1 mm Hg and 95°C. The absence of the solvent in the extracted material was confirmed by thermogravimetry



Figure 2-5.
Soxhlet apparatus for extraction of asphalt using toluene.



Figure 2-6.
Rotary evaporator for concentration of toluene asphalt extracts.

In a typical experiment 100g of mix was extracted using 500 ml of toluene. An average amount of 3g binder/100 g mix has been extracted. Based on these results an efficient technique for the extraction of asphalt cements from mixtures was developed as follows:

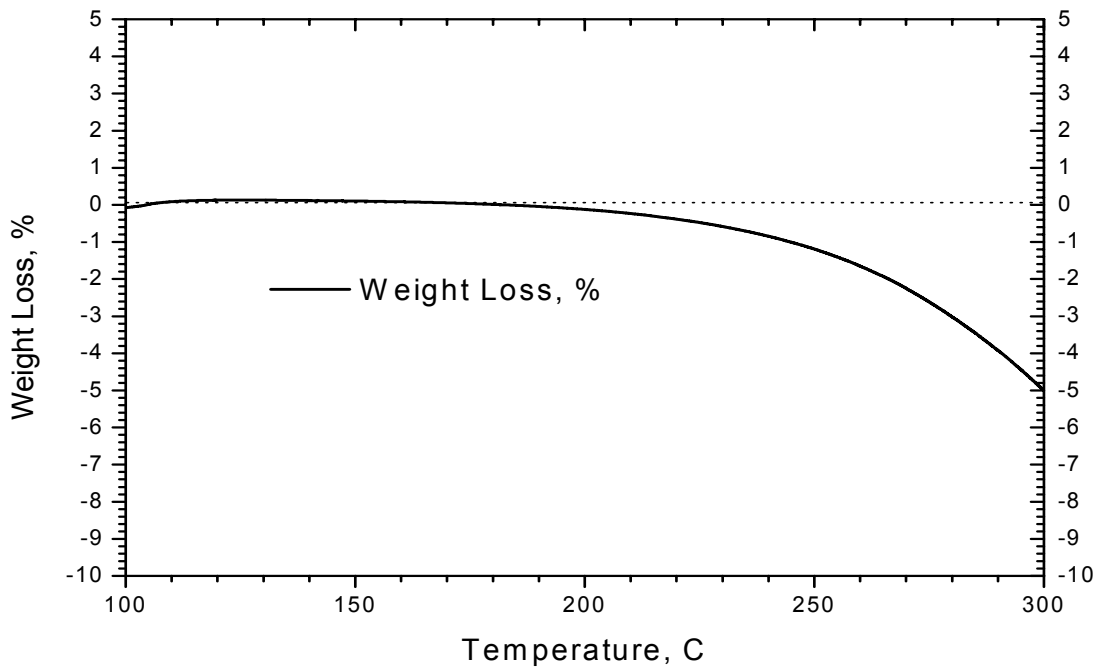


Figure 2-7
Percent weight loss versus temperature for PMAC sample.

In a typical run, 2-3 Kg of mix were placed in a large Soxhlet apparatus and extracted with 3 L of toluene at reflux under nitrogen until the toluene solvent siphoning from the extraction chamber was clear (12 to 18 hrs). The solution of asphalt cement in toluene was cooled to room temperature and then filtered to remove most of the fine particles of sand present.

The filtered solution was allowed to stand overnight, decanted, and concentrated under vacuum to approximately 0.5 L using the Büchi Rotavapor R200 rotary evaporator shown in Figure 2-6. The concentrated asphalt cement solution in toluene was then dried for 36 to 48 hours in a vacuum oven first at room temperature (ca. 24 hrs), then at 50°C for 12 hrs and finally at 115-120°C for the rest of the time. A yield of 60 to 90 g of dried asphalt cement was recovered from each batch. To ensure that all the solvent (toluene) was removed, a thermogravimetric analysis (TGA) was performed after each batch dried. A typical TGA curve is shown in Figure 2-7. Note that less than 0.1 percent of the sample evaporated at temperatures below 180°C.

CHAPTER 3*

SPECTROSCOPIC ANALYSIS

Introduction

Performances of asphalt pavements are directly related to chemical composition of asphalt binders the roads are made of.^{35, 52} Chemical composition of asphalts however changes during both long term and short term aging. Asphalts from different sources age differently. A major factor leading to the hardening and embrittlement of asphalt pavements is the reaction of asphalt with atmospheric oxygen. As proposed by Petersen²⁷, the hardening phenomenon is primarily a result of the formation in asphalt of polar oxygen containing functional groups that increase asphalt consistency through strong molecular interaction forces. Quantification of the oxygen uptake during aging is therefore a direct measure of the advancement of the aging process. Spectroscopic determinations (FTIR) and “wet chemistry” analysis (direct titration of functional groups) are the most used methods to this aim.⁵²

The polymer modifier used in this research is a poly(styrene-*b*-butadiene) triblock copolymer (SBS). It is synthesized through an anionic polymerization process, and the resulting block copolymer has the following structure:⁵³

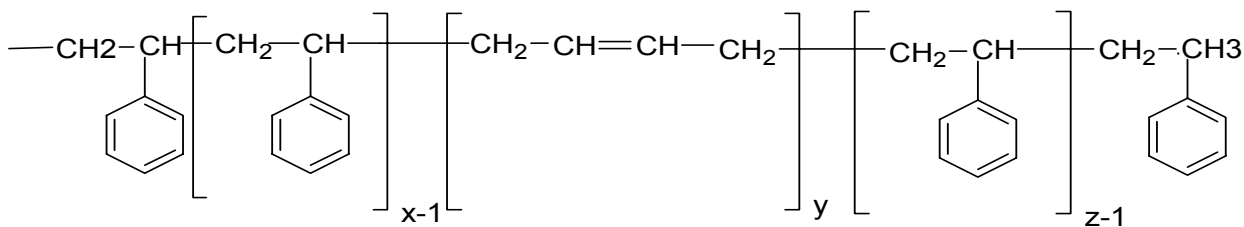


Figure 3-1.
The chemical structure of SBS tri-block copolymer

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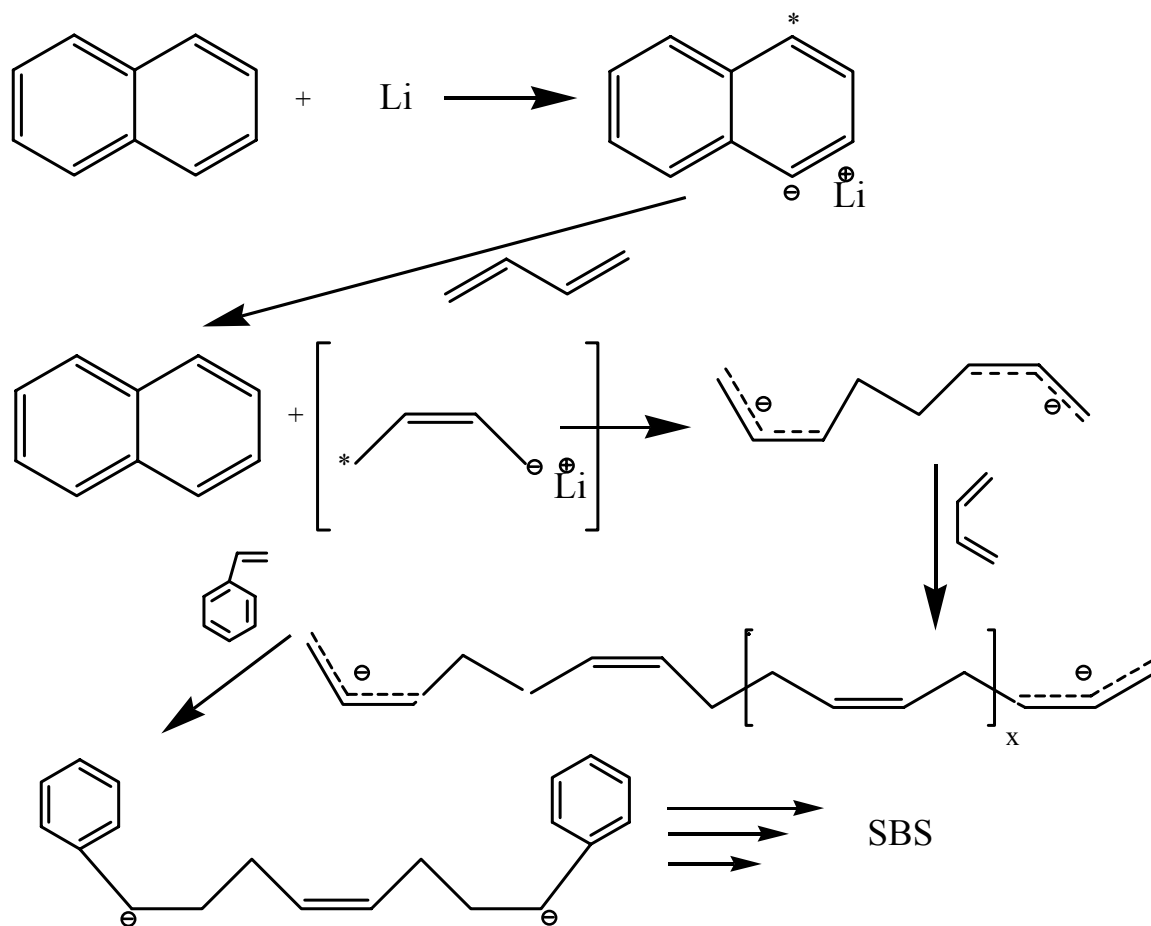


Figure 3-2.
Reaction Scheme 1.

◆ **Autoxidation of the SBS copolymer:**⁵⁴⁻⁵⁷ The facile autoxidation of the SBS copolymer allows it to serve as an antioxidant. The autoxidation is initiated by the abstraction of an allylic hydrogen as illustrated in scheme 2, reaction 1. Reaction of the allylic radical produced, with oxygen, yields peroxide radicals as shown in reaction 2. This is the first step of the propagation sequence. The propagation is completed when the peroxy radical abstracts hydrogen to produce a hydroperoxide and a second allylic radical as described in reaction 3.

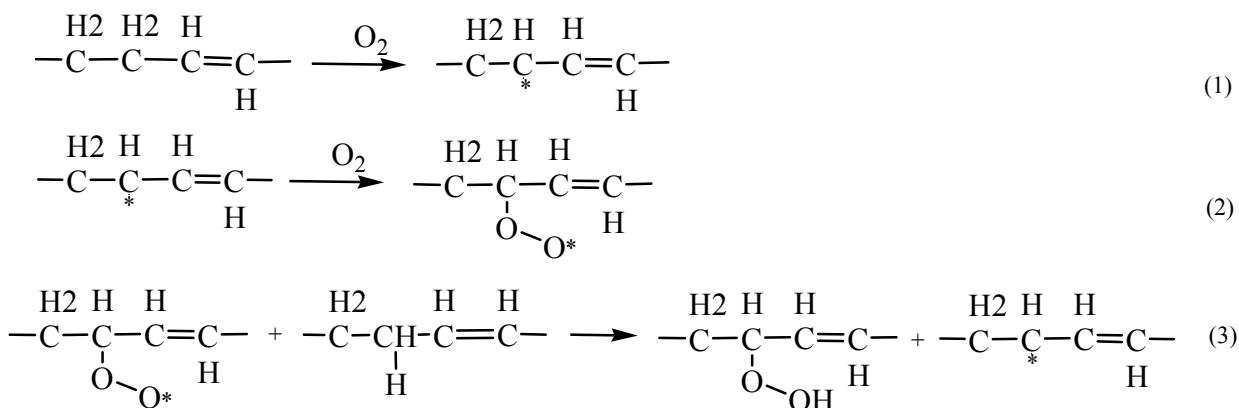


Figure 3-3.
Reaction scheme 2

◆ **Hydroperoxide Decomposition:**⁵⁴⁻⁵⁷ Metal ions present as impurities in the asphalt can serve as catalysts for the hydroperoxide decomposition reaction via a redox mechanism. Such a case is illustrated in reaction scheme 3. The metal ion is reduced and one oxygen radical is formed in the process (reaction 4), which reacts furthermore with a new polybutadiene chain to form a hydroxilic group at the allylic position, and a stable allylic carbon radical (reaction 5). A critical part of this is the fact that the oxygen radical can lead to chain scission as presented in reaction 6.

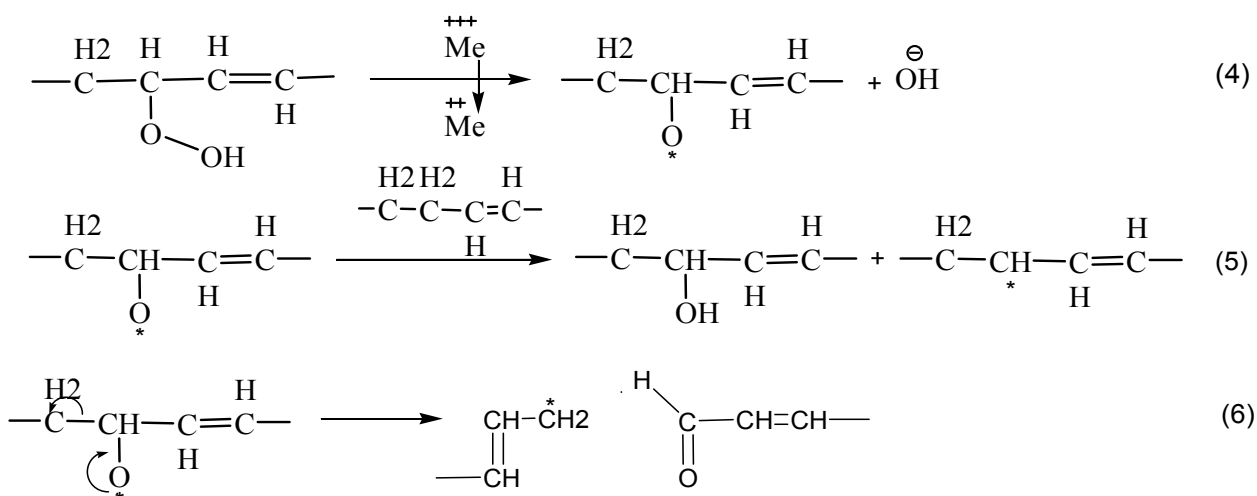


Figure 3-4.
Reaction scheme 3

Chain scission will lower the molecular weight of polybutadiene block and lead to a loss of mechanical properties. The aldehyde groups formed may be further oxidized by well known mechanisms to produce the carboxylic acid groups observed in the aged asphalt binder.⁵⁸

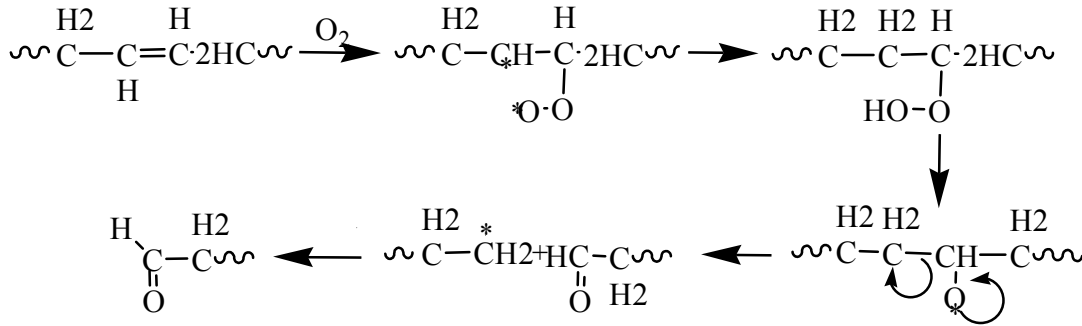


Figure 3-5.
The mechanism for aldehyde group formation in the aged asphalt binder

FTIR Measurements

The composition of the PMAC was studied using infrared (IR) spectroscopy. A *Fourier Transform Infrared (FTIR)* spectrometer uses the technique of Michelson interferometry. A beam of radiation from the source, S, is focused on a beam splitter constructed such that half the beam is reflected to a fixed mirror. The other half of the beam is transmitted to a moving mirror which reflects the beam back to the beam splitter from where it travels, recombined with the original half beam, to the detector, D (Figure 3-6).

The recombined beam passes through the sample before hitting the detector. The sample absorbs all the different wavelengths characteristic of its spectrum, and this subtracts specific wavelengths from the interferogram. The detector now reports variation in energy versus time for all wavelengths simultaneously. Energy versus time is an odd way to record a spectrum. Because **time** and **frequency** are reciprocals, a mathematical Fourier transform

function allows the conversion of an intensity-vs.-time spectrum into an intensity-vs.-frequency spectrum.

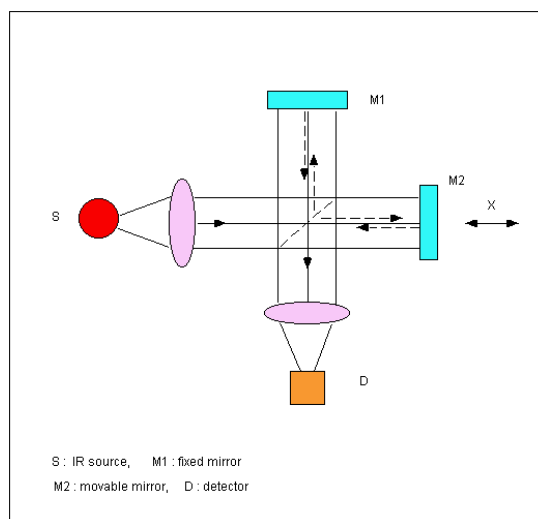


Figure 3-6.
Principle of an FTIR instrument

The IR intensity variation with optical path difference (interferogram) is the Fourier transform of the (broadband) incident radiation. A laser beam is superimposed to provide a reference for the instrument operation. The IR absorption spectrum can be obtained by measuring an interferogram with and without a sample in the beam and transforming the interferograms into spectra. Most spectra using electromagnetic radiation are presented with wavelength as the X-axis. Originally, IR spectra were presented in units of micrometers. However, a linear axis in micrometers compresses the region of the spectrum (10-15 μm) that usually has the largest number of peaks. Therefore, a different measure, the wave number (ν), was derived as follows: $\nu (\text{cm}^{-1}) = 10,000/\lambda (\mu\text{m})$. On the wave number scale (4000-400 cm^{-1}) the vibration of carbon dioxide, $\text{O}=\text{C}=\text{O}$, mentioned before is seen as a band at 2400 cm^{-1} . The C-H from C single bonds appears at around 2800-3000 cm^{-1} and the non-aromatic C=C double bonds absorb in the 900-1000 cm^{-1} region. The carbonyl C=O double bonds, of particular interest for the analysis

of asphalt oxidation, appear in the region of 1650-1800 cm^{-1} , with specific bands for acids (1650-1700 cm^{-1}), esters (1740-1750 cm^{-1}), aldehydes (1720-1750 cm^{-1}) and ketones (1720-1750 cm^{-1}). Also, aromatic rings show breathing vibrations centered at around 1600 cm^{-1} .

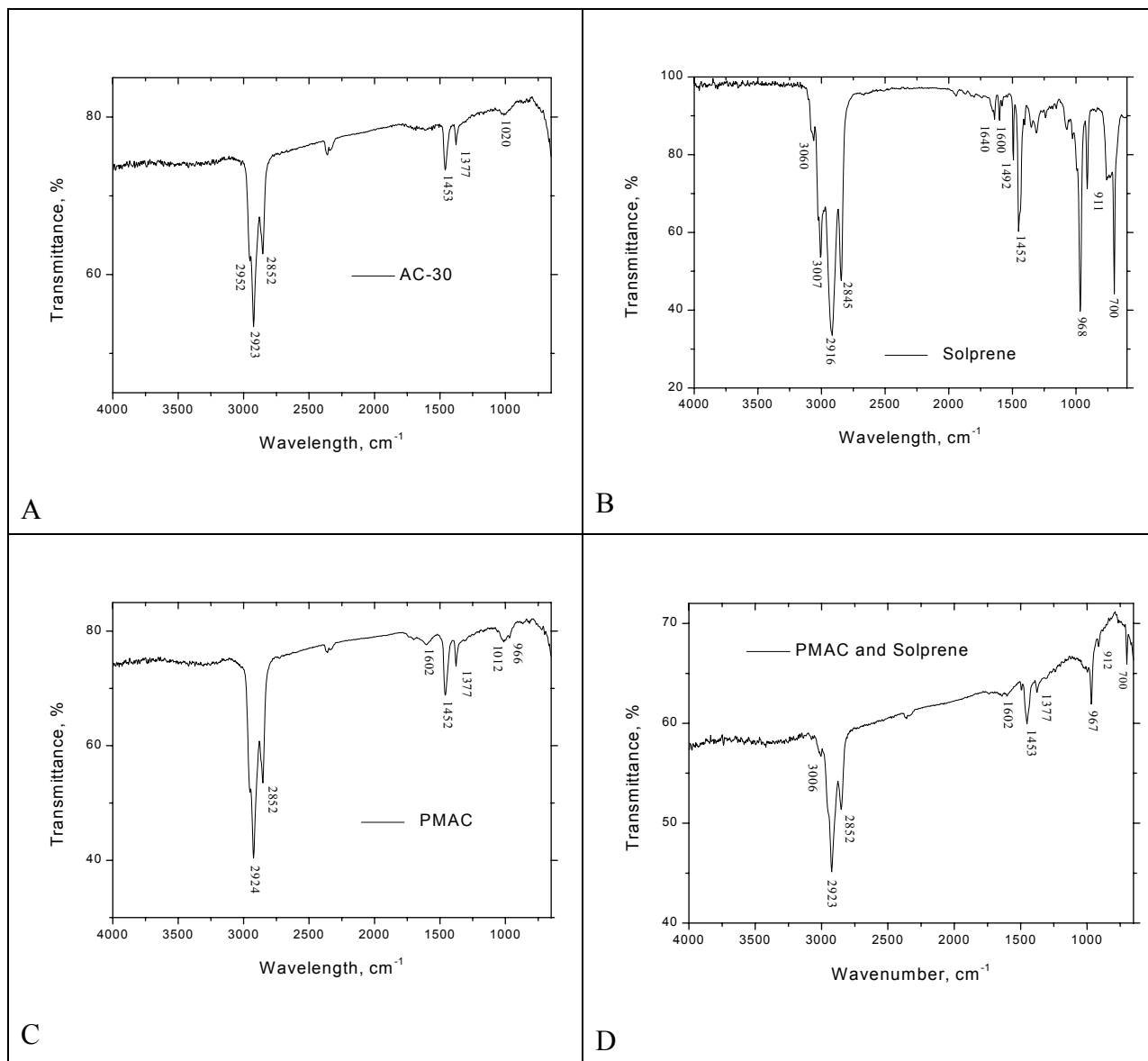


Figure 3-7.

FTIR spectra of PMAC components and of polymer spiked PMAC (film on NaCl plate)

The major bands in the parent AC-30 (Figure 3-7A) were identified as typical hydrocarbon absorbancies at 2952, 2923 and 2852 cm^{-1} . Weaker bands were noted at 1453 and 1377 cm^{-1} .

The polymer additive, an SBS rubber, exhibited a similar set of hydrocarbon bands (Figure 3-7B); however, one unique band at 966-968 cm^{-1} , corresponding to residual unsaturation, was noted. Using this band it was possible to detect the presence of the polymer in the PMAC (Figure 3-7C). To confirm that this band was indeed characteristic of the polymer, additional quantities of polymer were added to PMAC and a corresponding increase in the band intensity at 966 cm^{-1} was observed (Figure 3-7D).

Aging is reflected in the infrared spectra of asphalts by multiple peaks centered around 1698 cm^{-1} , which correspond to carbonyl (C = O) absorptions of oxidized species, such as ketones or carboxylic acids.^{7, 59} By comparing the intensity of the 1698 cm^{-1} region to that of 1600 cm^{-1} , which is attributed to aromatic ring vibrations, the relative degree of oxidation of the samples can be estimated. The more oxidized the asphalt (e.g., PAV aged), the more intense the 1698 cm^{-1} peak becomes and the corresponding 1698/1455 cm^{-1} ratio increases. Figure 3-8 presents the FTIR spectra of un-aged and PAV aged asphalt samples. Carbonyl species are present also in the asphalt, but their concentration is very small. The 1695/1455 cm^{-1} ratio calculated from the spectrum is not relevant due to the lack of oxidized species. After PAV aging, the sample was clearly oxidized; the 1698/1455 cm^{-1} ratio is 0.53 as shown in Figure 3-9. The higher auto-oxidative sensitivity of PMAC suggests that the polymer additive is behaving as a sacrificial antioxidant. The allylic positions adjacent to the C=C double bonds within polybutadiene blocks can readily react with oxygen, particularly at elevated temperatures ($t > 100^\circ\text{C}$), bringing about a significant increase of carbonyl species and a concomitant cleavage of the polymer backbone. The reduction in molecular weight can be detected using gel permeation chromatography (*vide infra*).

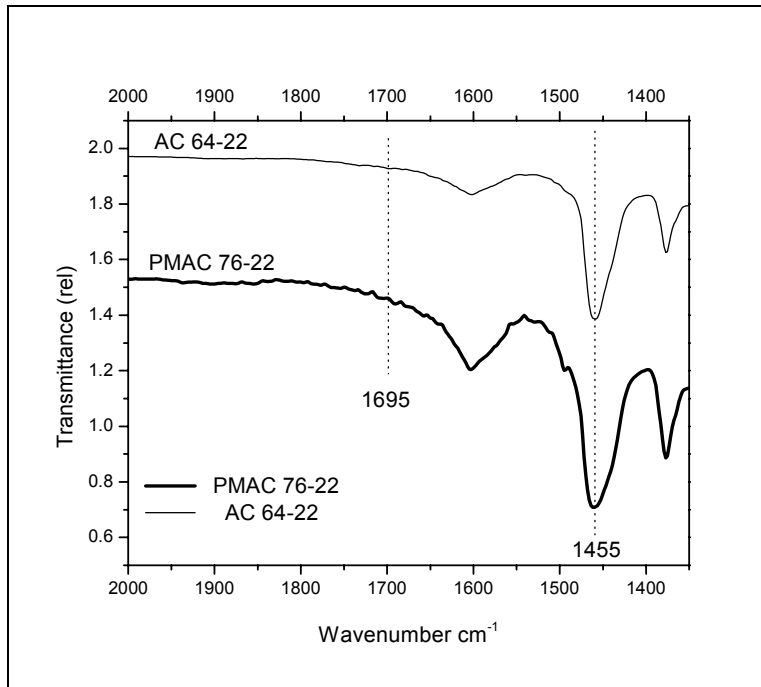


Figure 3-8.
FTIR spectra of asphalts before dry PAV aging

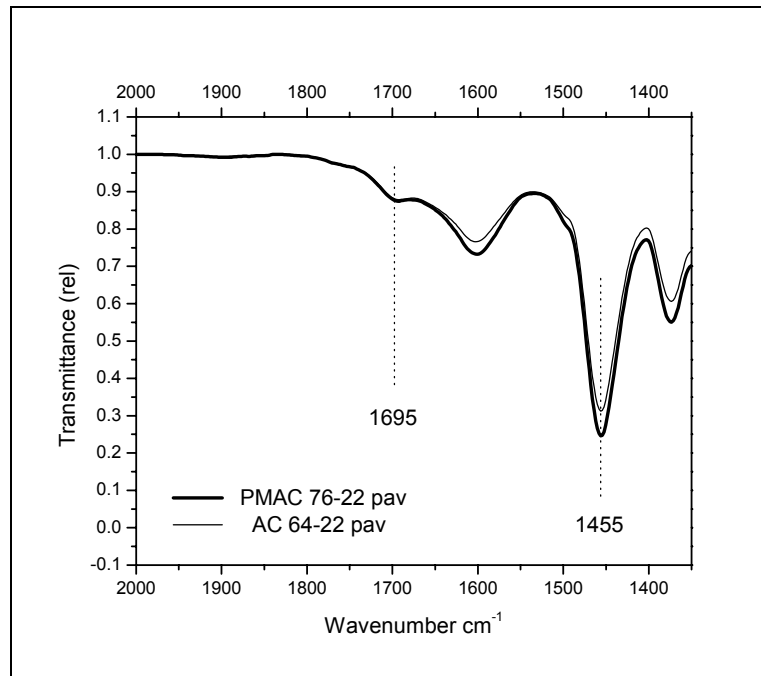


Figure 3-9.
FTIR spectra of asphalts after dry PAV aging

The uptake of oxygen became more relevant after extensive PAV aging, with a 1695/1455 cm^{-1} peak ratio of 2.5 after 2xPAV operations (40 hrs) in presence of water (Figure 3-10). The water interferes with oxidation process perhaps by forming an asphalt-oxygen-water complex.¹⁹ A typical FTIR spectrum is shown in Figure 3-11. In an attempt to quantify the carboxylic acid groups after aging, solutions of benzoic acid in asphalt of known concentration were analyzed in order to build a calibration curve (Figure 3-12). A polynomial correlation between the absorbance ratios and carboxylic acid content was observed. While the same trend was observed as that indicated by the ratio of 1695/1455 cm^{-1} absorption peaks, the results were somewhat different from that obtained by potentiometric titration (Table 3-1). One reason might be the presence of other carbonyl species in FTIR spectra which were not accounted by titration. As shown by data listed in Table 3-1, the content of carboxyl groups of field aged asphalt samples after 5 and 7 years on the road were close but less than that of the 1.0xPAV sample aged in absence of water.

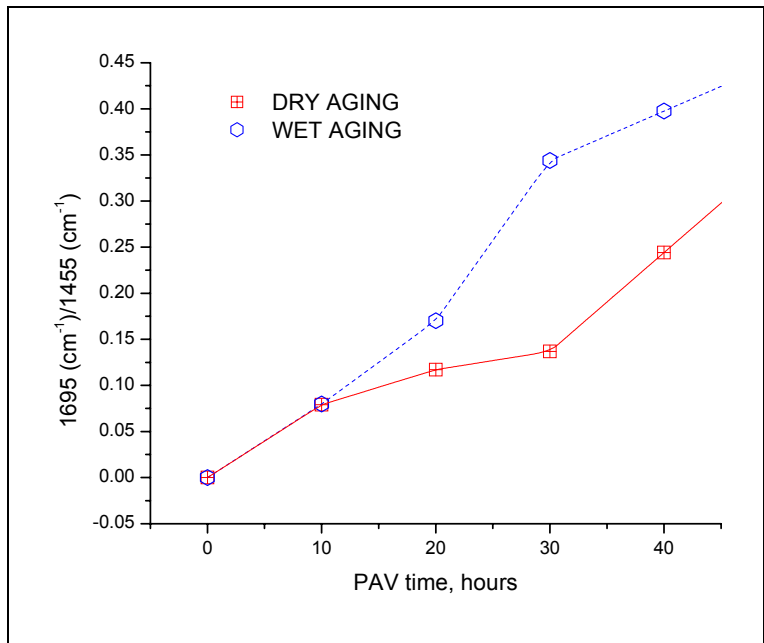


Figure 3-10.

Increasing of carbonyl species of asphalts samples after dry and wet PAV aging as indicated by the ratio of peak absorption

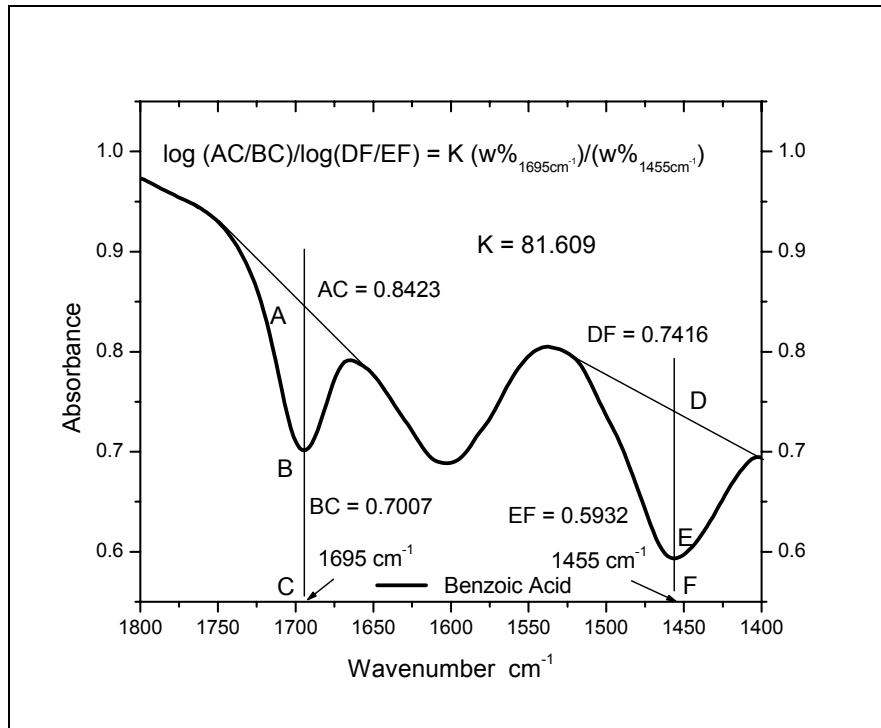


Figure 3-11.

Illustration of method for quantifying carboxylic acid content using benzoic acid

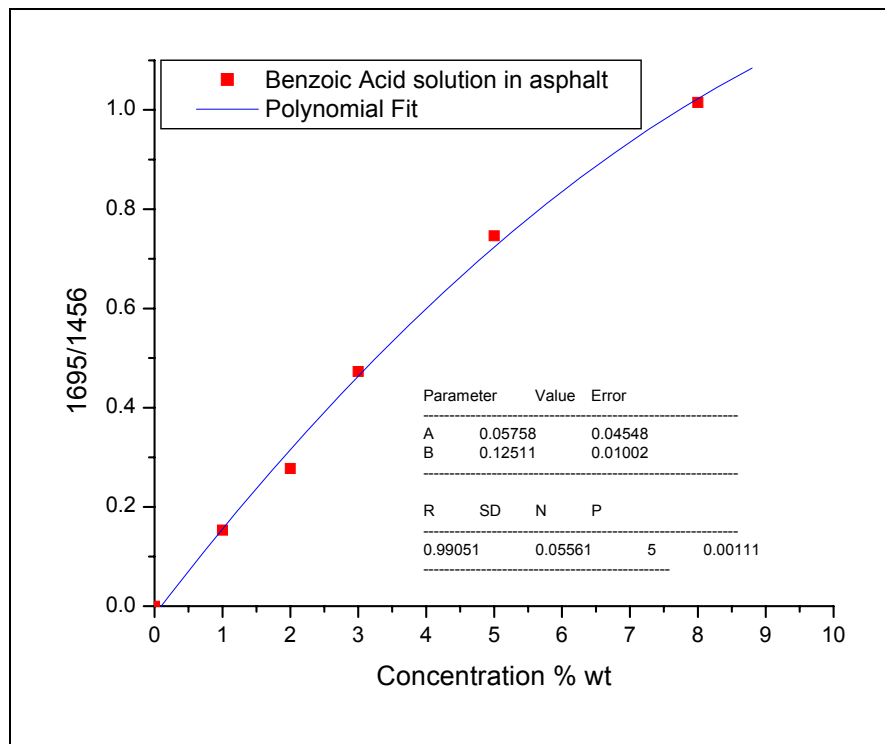


Figure 3-12.

Signal ratio 1695/1455 FTIR bands versus wt% benzoic acid solution in asphalt.

The laboratory results of PAV samples aged in presence of water did not match the data of asphalts extracted from aged pavements; after only 10 hrs of treatment (0.5xPAV) the carboxylic acid content exceeded that of the longest field aged asphalt.

A similar FTIR analysis was made to quantify double bond content of polybutadiene blocks in PMAC samples before and after aging. The building of calibration curve was based on the vibrations of unsaturated carbon bonds at 966 cm^{-1} relative to the same 1455 cm^{-1} peak (Figure 3-13). Analysis of data obtained for PAV aged samples indicated a rapid decrease of unsaturation both for dry and wet aged asphalt samples (Figure 3-14).

Table 3-1. Results of non-aqueous potentiometric titration of acid groups in asphalts

Asphalt Sample	Aging Time	Acid Groups Content (meq/g)
0.5xPAV Dry	Lab 10 hrs	0.01543
0.5xPAV Wet	Lab 10 hrs	0.03253
1.0xPAV Dry	Lab 20 hrs	0.02953
1.5xPAV Dry	Lab 30 hrs	0.03060
1.5xPAV Wet	Lab 30 hrs	0.03663
I-55 Extract	Field 3 years	0.02082
I-55 Extract	Field 5 years	0.02293
I-55 Extract	Field 7 years	0.02450

These results correlated well with GPC data reported previously which indicated a severe diminution of molecular weight of polymeric species after aging.⁶⁰ However, it seems that for a reduced aging time (10 hrs) the water retarded the oxidation of SBS double bonds (Figure 3-14).

Thermo-oxidative degradation of SBS elastomers occurs within the polybutadiene segment only; no oxidation of the polystyrene segments is expected.⁵⁹ After extensive oxidation the polymer is effectively degraded and can no longer be detected in the aged binder.

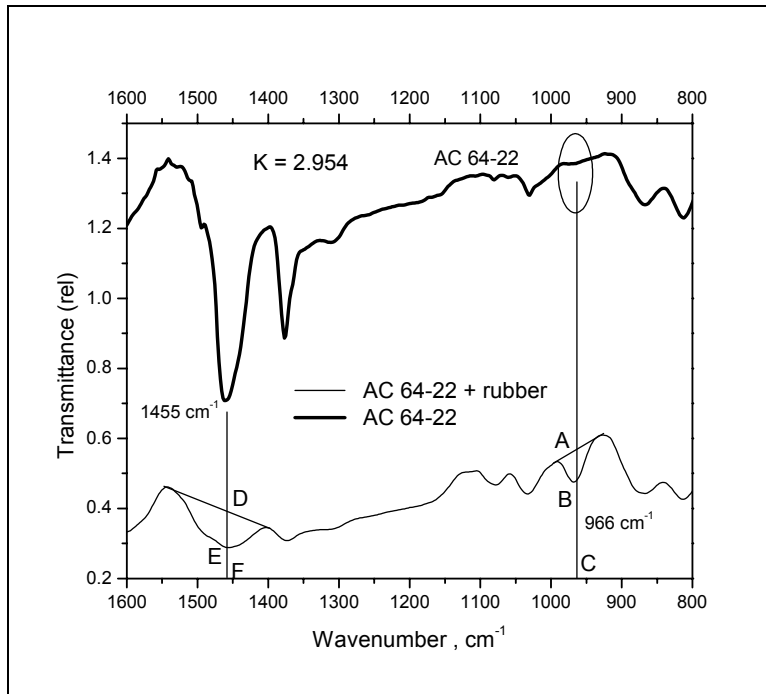


Figure 3-13.

Illustration of method for quantification of double bonds using the 966 cm^{-1} peak absorption of SBS rubber dissolved in AC 64-22 asphalt cement

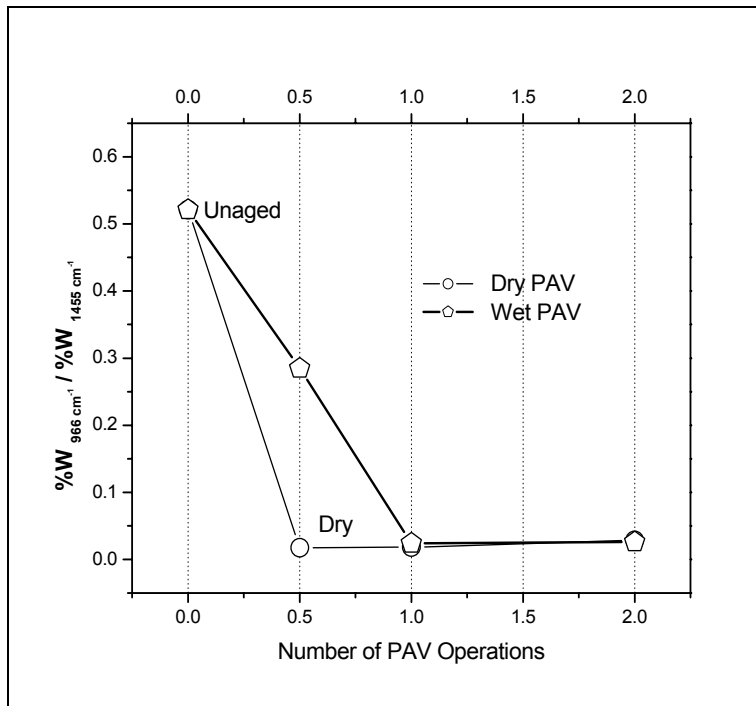


Figure 3-14.

Diminution of PMAC unsaturation after dry and wet PAV aging

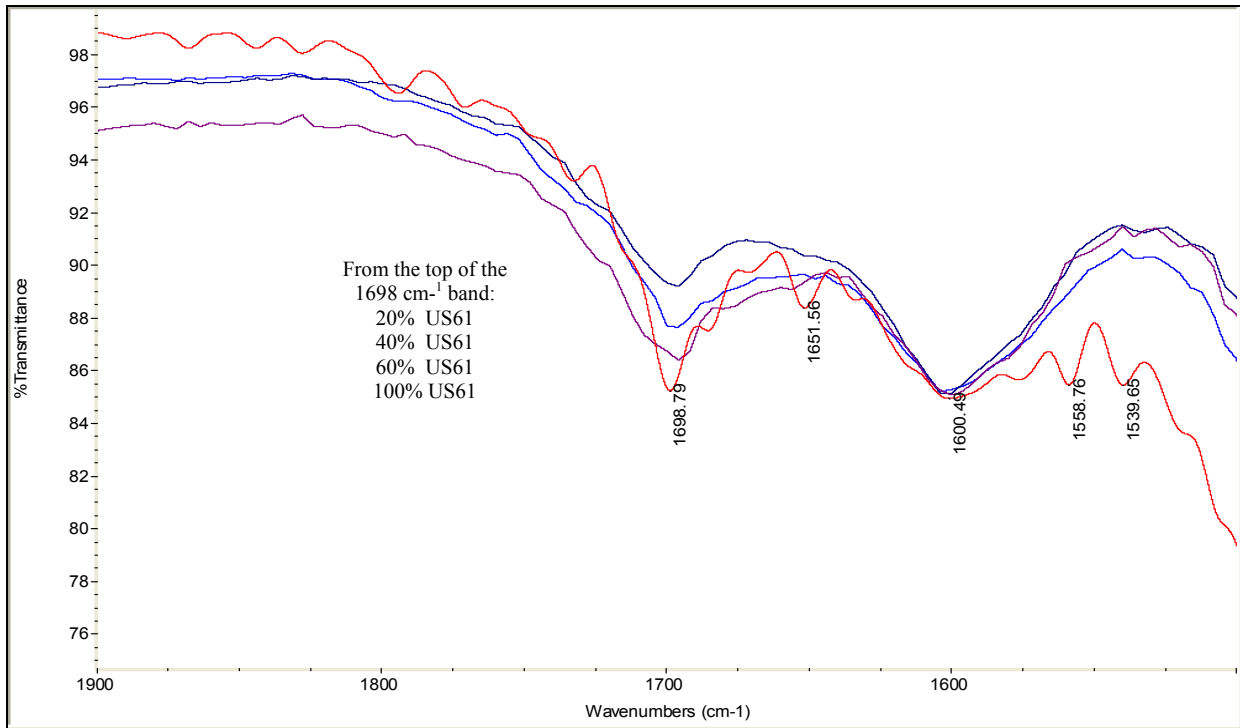


Figure 3-15
 Comparative FTIR spectra of blends made with PMAC containing 20, 40, and 60 percent US61 binder (films on NaCl plates).

Although oxidation of the asphalt components may be retarded by the presence of the polymer, age hardening continues to occur.⁷ The ¼ inch bump grind surface binder exhibits a higher extent of oxidation than the laboratory aged samples (PAV aged PMAC). This can be clearly observed by observing the 1698/1600 ratio which is A:B = 1.76. The extensive oxidation is a result of the surface being directly exposed to the moisture and oxygen in the air as well as sunlight and traffic related mechanical stresses. Dilution with virgin PMAC effectively reduced the concentration of aged material; the 1698/1600 ratio decreased to 1.58, 1.33 and 0.96 for samples containing 60 percent field aged binder, 40 percent field aged binder, and 20 percent field aged binder, respectively (Figure 3-15).

GPC Measurements

Size-exclusion chromatography (SEC), also called gel-filtration or gel-permeation chromatography (GPC), uses porous particles to separate molecules of different sizes. It is generally used to separate and to determine molecular weights and molecular weight distributions of polymers. A mechanical pump *B* (Figure 3-16) provides an eluting solvent from reservoir *A* to push the sample along in columns *D*.

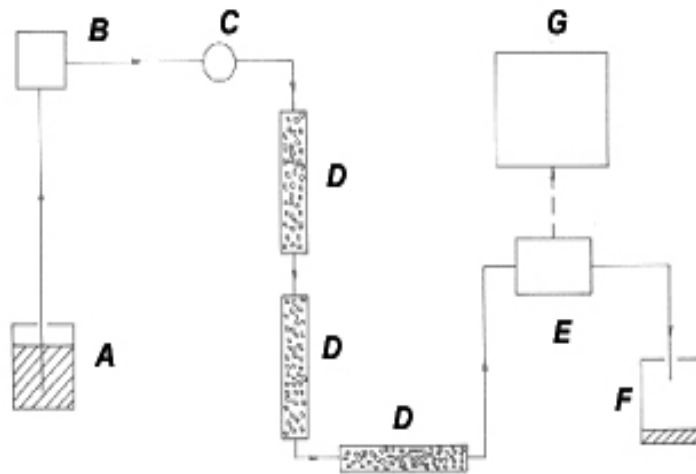


Figure 3-16.

Schematic illustration of a GPC apparatus: *A*, solvent reservoir; *B*, solvent pump; *C*, injection valve; *D*, GPC column; *E*, detector; *F*, waste solvent/solution reservoir; and *G*, computer.

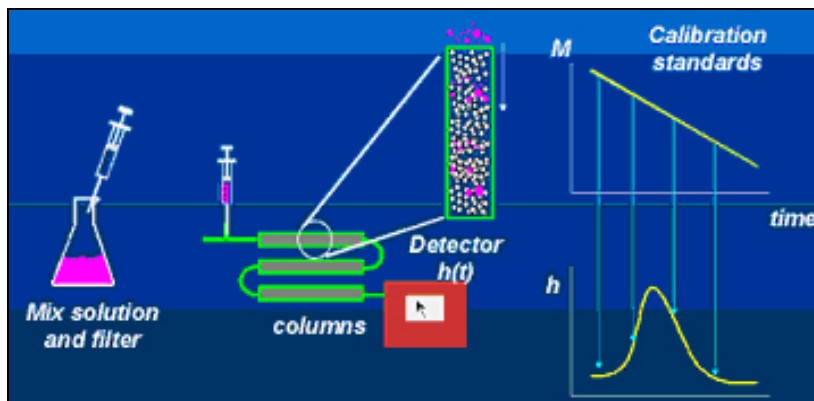


Figure 3-17.
General scheme for a GPC experiment.

Determination of molecular mass of polymers needs a calibration of columns with similar polymeric species of known molecular mass (Figure 3-17).

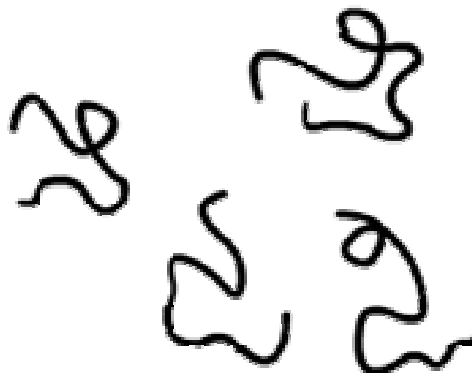


Figure 3-18.
Individual polymer molecules in dilute solutions

Experimentally, a GPC analysis for determination of molecular mass of polymers starts with the preparation of a dilute polymer solution (e.g., 0.25%) and filtration of the solution. The solution is then injected into the column at the time $t = 0$ min and some characteristics of the eluate from the columns, such as absorption of UV light or the refractive index are compared in the detector to that of the pure solvent. The peak height (h) is related to the polymer sample concentration of molecular species of mass M as determined from the calibration curve (Figure 3-17). Low percent weight polymer solutions should be analyzed by GPC because in dilute solutions the polymer molecules are not entangled (Figure 3-18) and can be separated as individual species.

In more concentrated solutions the macromolecules can entangle and form aggregates stabilized by secondary forces (such as hydrogen bonding or π - π interactions between aromatic nuclei), as depicted in Figure 3-19.

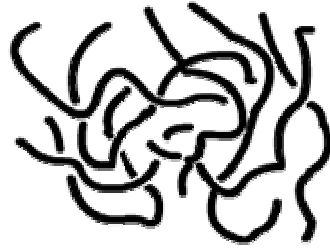


Figure 3-19.
Aggregated polymer molecules formed in concentrated solutions.

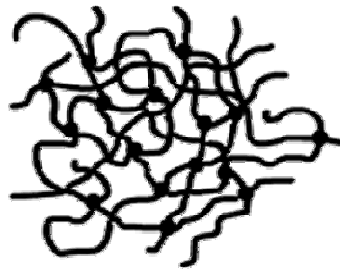


Figure 3-20.
Crosslinked polymer molecules

Such aggregates can appear larger than the pore size and will be excluded, giving an erroneous indication of very high molecular mass for the analyzed polymer. If the polymer molecules are linked through stable chemical bonds, e.g., covalently bonded, crosslinked “aggregates” are formed which are not soluble. Even for a very high solvent:polymer ratio (e.g., > 1,000), the crosslinked polymer (Figure 3-20) does not dissolve and forms gels by absorbing the solvent. Insoluble polymeric species and gels are precluded from entering the columns through filtration through a short guard column.

We found that the polymer and asphalt components of PMAC could be separated using gel permeation chromatography (GPC). Solutions of the asphalt samples were prepared in tetrahydrofuran (THF) and analyzed. The parent AC-30 eluted in a relatively broad band

centering at an elution volume of 27.9 mL or at a molecular weight of ~ 1000 Daltons (Figure 3-21A). The SBS sample eluted at 20.95 mL (Figure 3-21B), which corresponds to a molecular weight of 110,000 Daltons.

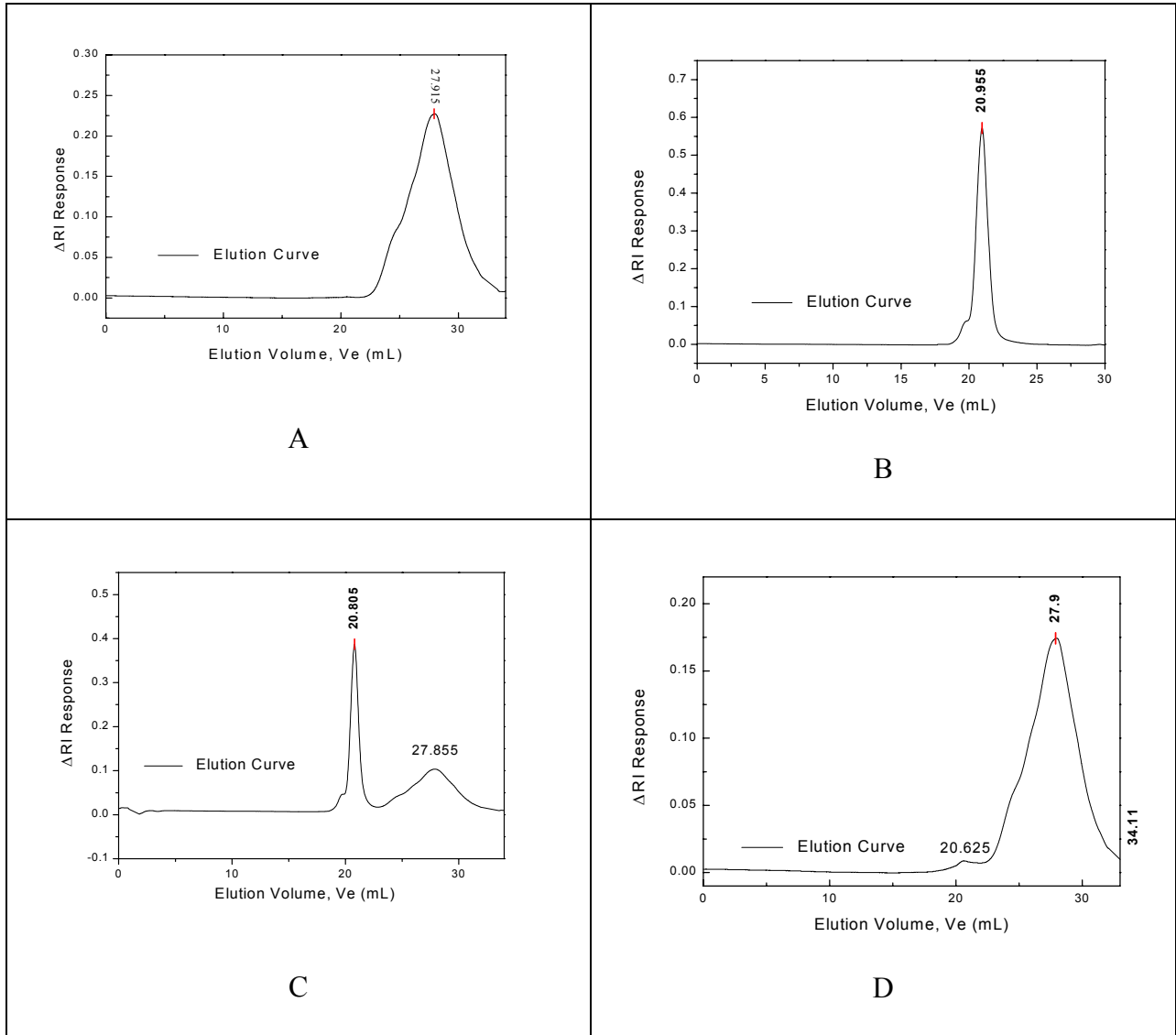


Figure 3-21.

GPC elution peaks of the base asphalt cement for PMAC (A), SBS polymer (B), 1:1 blend of base asphalt and SBS (C), and PMAC samples.

The large differences in the molecular weights between the asphalt and polymer components allowed baseline separation of the two components in the GPC chromatogram of a

prepared mixture containing approximately 15 percent SBS (Figure 3-21C). When the technique was applied to the PMAC sample, the SBS component was clearly separated with a peak centering at 20.62 (Figure 3-21D). The lower elution volume corresponds to a slight increase in the polymer molecular weight, which might have been occurred during the plant preparation of the polymer modified asphalt.

A control sample of AC-30 containing 3% SBS was prepared and submitted to TFOT. A new set of columns has been used to develop the GPC chromatogram (Figure 3-22). Therefore, the elution volumes are slightly different from those reported above for asphalts and SBS samples. The parent asphalt cement (AC-30) eluted in a relatively broad band centering at an elution volume of 21 mL. Each peak in the GPC chromatogram is identified both the elution volume and the corresponding molecular weights. In this particular sample, the polymer peak is obvious at an elution volume of 14.2 mL, which corresponds to a peak molecular weight of 120,000 daltons.

For the analysis of the field aged US61 binder (surface sampled asphalt, top ½ in, labeled as US-61S) the new set of columns was used. The parent asphalt cement (AC-30) eluted in all cases in a relatively broad band centering at an elution volume between 21.75 mL for US-61S sample and 21.95 mL for PMAC, or at a molecular weight of the order of 10^3 Daltons (Figure 3-23). As expected, aging increased slightly the mean molecular weight of asphalt components, as seen by the shift of the peak of PAV aged PMAC to a slightly lower elution volume (21.90 mL). The large differences in the molecular weights between the asphalt and polymer components allowed again baseline separation of the two species in the GPC chromatogram. The polymer species from PMAC eluted at 15.2 mL (Figure 3-24), which corresponds to a molecular weight of 110,000 Daltons.

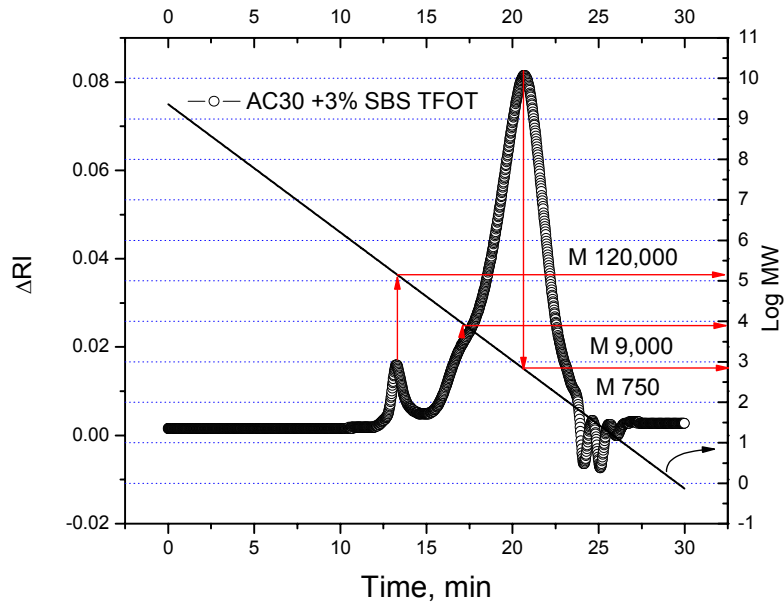


Figure 3-22.
GPC chromatogram of a blend of 3% SBS with AC-30 after TFOT

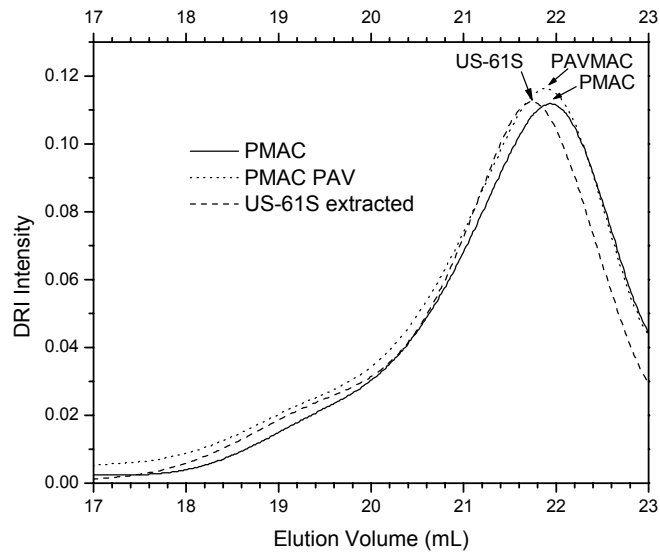


Figure 3-23.
GPC elution peaks of the base asphalt cement for PMAC, PAV aged PMAC, and US-61S binder sampled from the road surface.

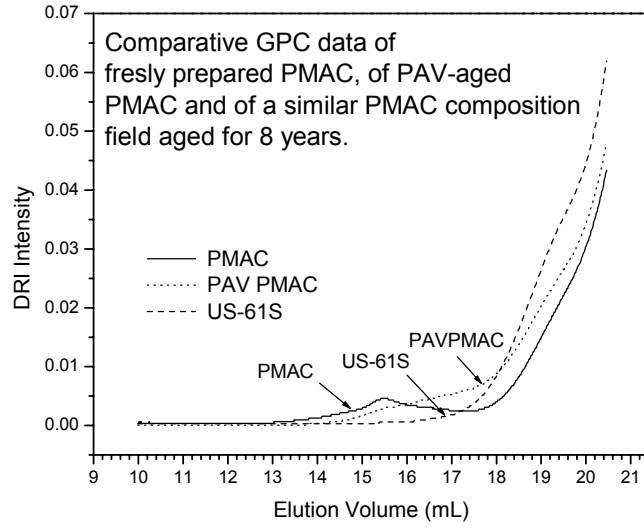


Figure 3-24.
 GPC curves at low elution volumes (i.e., high MW) for PMAC, PAV aged PMAC and US-61S binder samples.

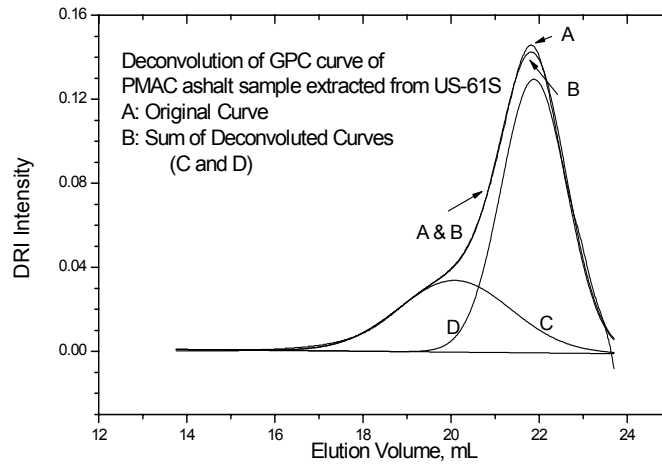


Figure 3-25.
 Deconvoluted GPC curves of PMAC, PAV PMAC and US61S binders.

The PAV aging process caused a severe oxidation of the PMAC polymer molecules, broadening the peak from 15.2 mL towards higher elution volumes, or lower molecular

weights. At the same time, the chromatogram of the US61 surface sampled asphalt showed none of any high molecular species and only one broad shoulder around 19.5 mL (Figure 3-24). No residual polymer could be detected in the US61S bump grind sample even after deconvolution of peaks (Figure 3-25). Presumably an extensive oxidation of molecular species of the base asphalt as well as polymer degradation occurred in the field aged samples taken from the road surface.

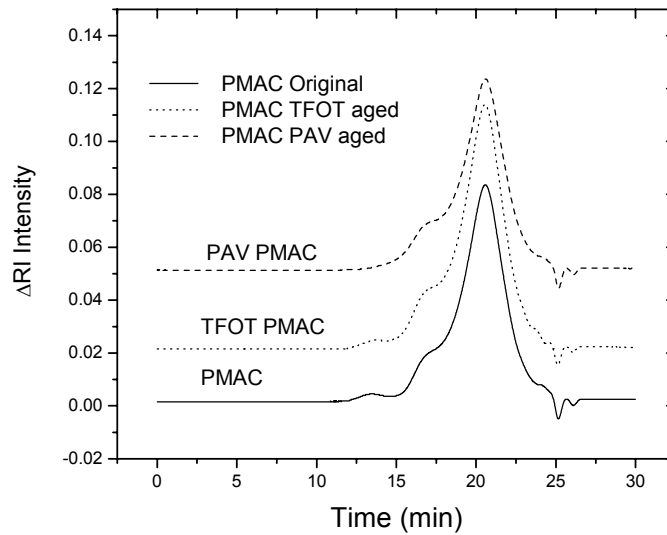


Figure 3-26
GPC curves for PMAC and its TFOT and PAV aged species.

In an effort to ascertain the fate of the polymer additive during oxidation (aging), a PMAC blend containing 3 wt% SBS was prepared and subjected to TFOT and PAV conditions. At the same time, a new US61 roadway core sample (labeled as US61C) was taken from beneath the road surface (2 in). Because a new set of GPC columns were used, analysis included the original PMAC binder and its TFOT and PAV aged species. Aging affected dramatically the mass of polymeric species (Figure 3-26).

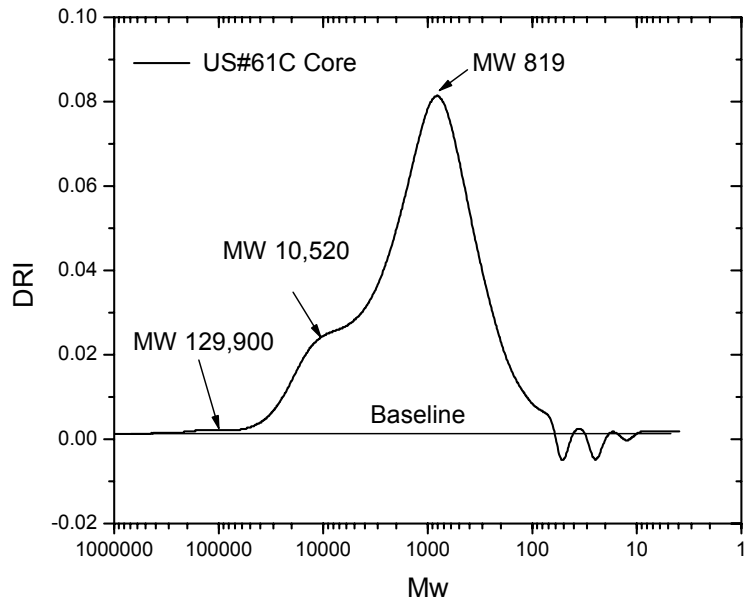


Figure 3-27
 GPC curve of the binder extracted from the US-61C core sample taken from beneath the road surface plotted vs. the MW calibration scale.

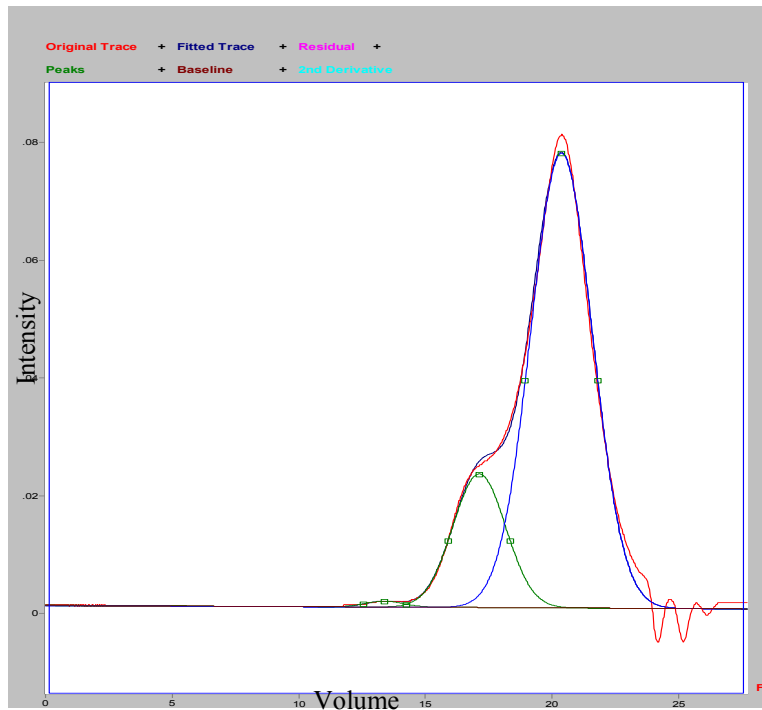


Figure 3-28
 Deconvoluted GPC curve of the binder extracted from the US-61C core sample taken from beneath the road surface showing the peak corresponding to polymeric species.

These preliminary MW data on lab and road aged samples show clearly that the current PAV protocol for aging of asphalt cements containing polymeric species, such as SBS, does not accurately reflect the real process of long term aging. Further studies to determine the fate of the polymer as the asphalt ages are on-going.

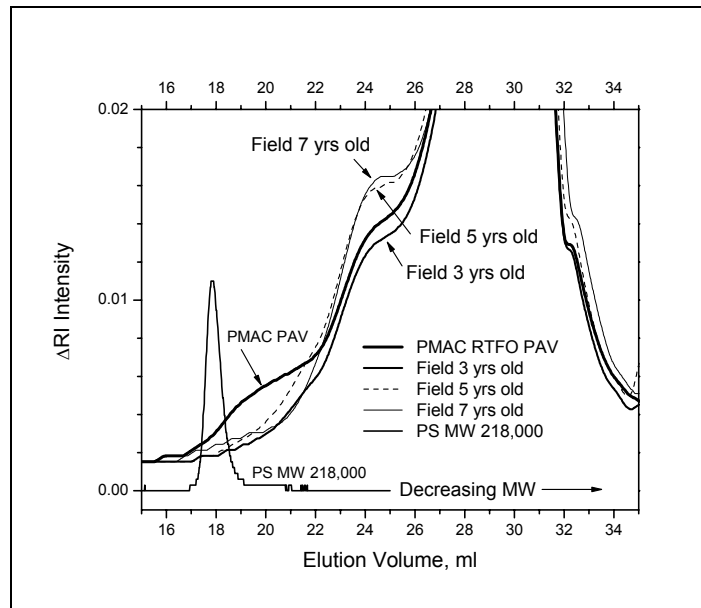


Figure 3-29.
GPC traces of asphalt samples extensively aged on the road

Besides the degradation of polymeric species to lower MW, weathering of the base asphalt cements result in a significant increase of large molecular size (LMS) species seen at around 10^4 Dalton in Figure 3-22 and a significant decrease of medium and small molecular size species.⁶¹ This shift is clearly represented by the results of the GPC analysis of asphalts extracted from core samples taken after years of aging on the road (Figure 3-29). Polymeric SBS species, still clearly present after PAV aging at MW of the order of 10^5 Daltons (a polystyrene standard with molecular weight of 2.18×10^5 Daltons is shown for comparison), diminished drastically after years of service on the road, while the large molecular weight components (asphaltenes) of the binder itself increased the intensity of LMS species of 10^4

Daltons: the longer the aging time, the higher the concentration of LMS components. This gradual increase of LMS species over the years indicates that after 7 years of service the asphalt hardening (not necessarily only through oxidation processes, as mentioned above) might not be over. Asphaltene aggregation could continue at a slower pace as aging advances.

CHAPTER 4[†] THERMAL ANALYSIS

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) has proved to be a very useful technique for estimating both the crystalline fraction and the glass transition temperature (T_g) of asphalt samples. F. Noel and L. W. Corbett obtained DSC thermograms of asphalts over a broad range of temperature, enunciated a need to establish a consistent thermal history prior to comparing different asphalts, and quantified the crystalline components.⁶² Blanchard et al. described techniques for measuring glass transition temperatures of asphalt fractions.⁶³ Claudy et al. devoted great efforts to studying the crystallized fraction in asphalt.⁶⁴ Daly et al. showed that the extent of crystallinity of a given asphalt binder can be enhanced by the addition of linear hydrocarbons of similar molecular weight.³⁸

Melting of AC-30 and PMAC crystalline paraffinic species was investigated by DSC in the temperature range of 15 to 100°C. The main melting process for an AC-30 sample was observed between 40 to 73°C, with a couple of peaks at 54 and 67°C, respectively (Figure 4-1). The corresponding heat (enthalpy) of fusion totaled 0.33 mJ/mg, which corresponds to a very low amount of crystalline paraffins in the asphalt composition (melting of paraffinic species 100 percent crystalline, such as linear polyethylene, requires an enthalpy of 200 mJ/mg).

Residual crystallinity of AC-30 is still detected in PMAC material after compounding AC-30 asphalt with SBS rubber (Figure 4-2). Comparatively, the heat of fusion is less (smaller

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integration area) than that of pure AC-30, but the transition temperatures are the same, i.e., the same crystalline species are present in both materials.

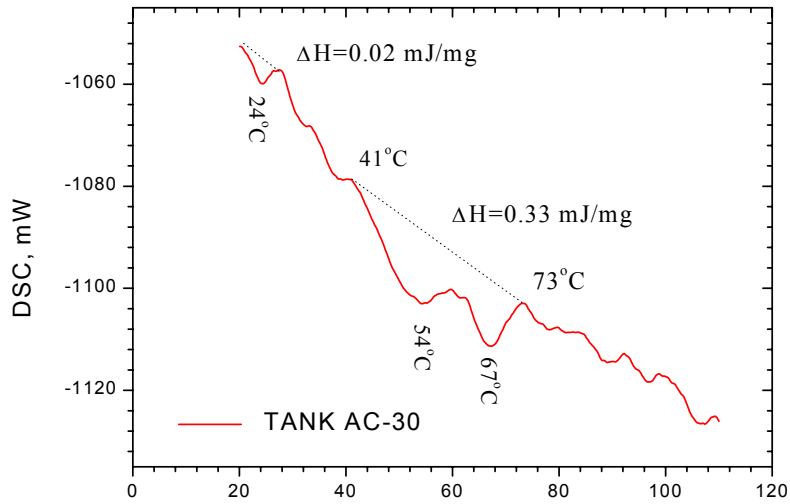


Figure 4-1.
DSC thermogram of AC-30 material.

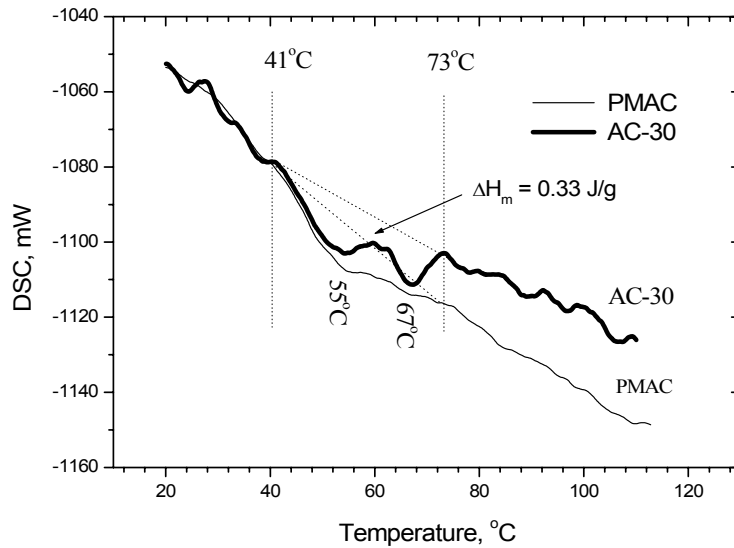


Figure 4-2.
Comparative DSC data of AC-30 and PMAC.
Traces were normalized to 10 mg for quantitative representation.

A DSC thermogram of the SBS rubber exhibited only the glass transition, T_g , due to polystyrene blocks at ca. 100°C since the T_g of the polybutadiene blocks falls below the range of temperatures studied. (Figure 4-3).

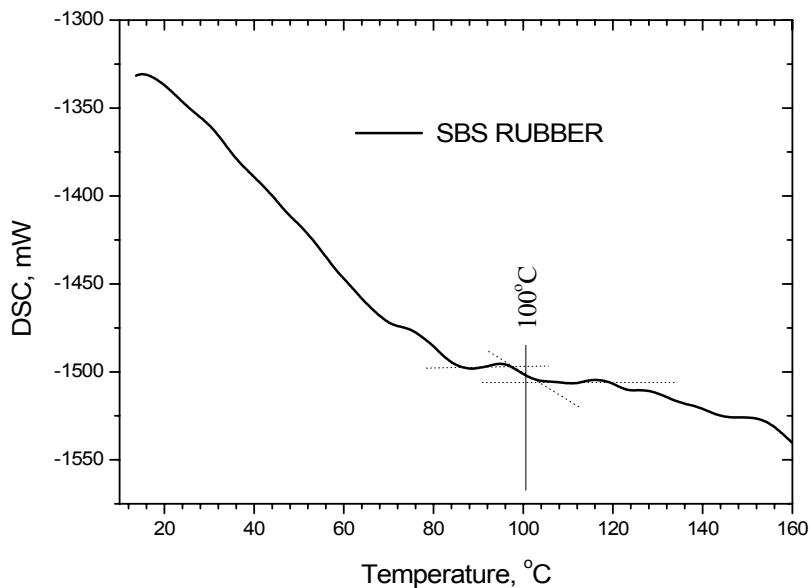


Figure 4-3
DSC thermogram of SBS styrene-butadiene block copolymer.

PAV aging reduced the paraffinic crystallinity of PMAC to one half that of the virgin sample ($\Delta H_m = 0.16$ J/g, Figure 4-4), rendering a material with good low temperature ductility (see below). On the other hand, the field-aged US61 binder, hard and brittle as compared to PAV PMAC sample (*vide infra*), was characterized in the same temperature domain by a rather high paraffinic content ($\Delta H_m = 0.58$ J/g, Figure 4-5). Moreover, the blends containing 20 to 60 percent US-61S binder and PMAC, all hard and brittle at low temperatures as seen by force ductility measurements, had a high paraffinic content, much higher than that given by the

simple computation based on their composition. For example, the blend with 60 percent PMAC and 40 percent US-61S material should have a total content of paraffins melting above 30°C with a enthalpy no higher than 0.43 J/g. However, the melting enthalpy as given by DSC was much higher ($\Delta H_m = 0.62$ J/g, Figure 4-6), indicating that, in fact, the US-61S components seeded the crystallization of PMAC paraffinic species. Therefore, despite of a high PMAC content, the blends with the field aged US-61S binder will display an unexpected brittleness at low temperatures.

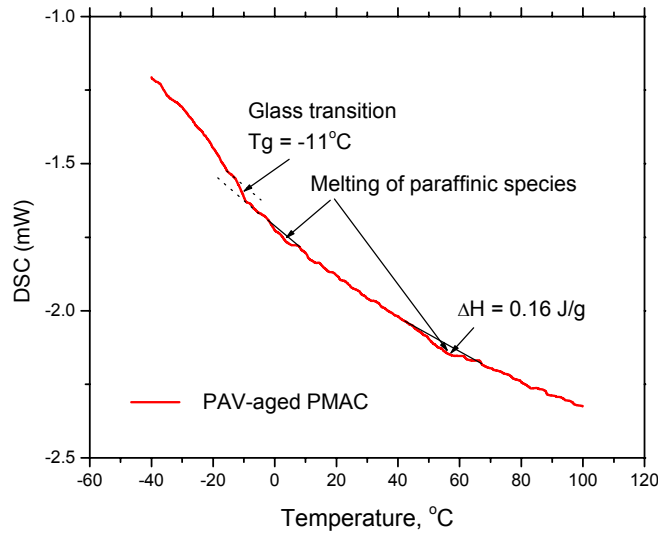


Figure 4-4
Glass transition and paraffinic crystallinity of PAV aged PMAC

This brittleness is related also to mobility of asphalt species as reflected by the glass transition, T_g , i.e., the higher the T_g , the more brittle the binder at low temperatures. As expected from mechanical measurements, the glass transition of US-61S binder ($T_g = 4.5^\circ\text{C}$, Figure 4-5) is higher than that of PAV aged PMAC ($T_g = -11^\circ\text{C}$, Figure 4-4), and

correspondingly, the T_g of the blends of US-61S and PMAC are in the range of these two temperatures, viz., the higher the US-61S content, the higher the glass transition

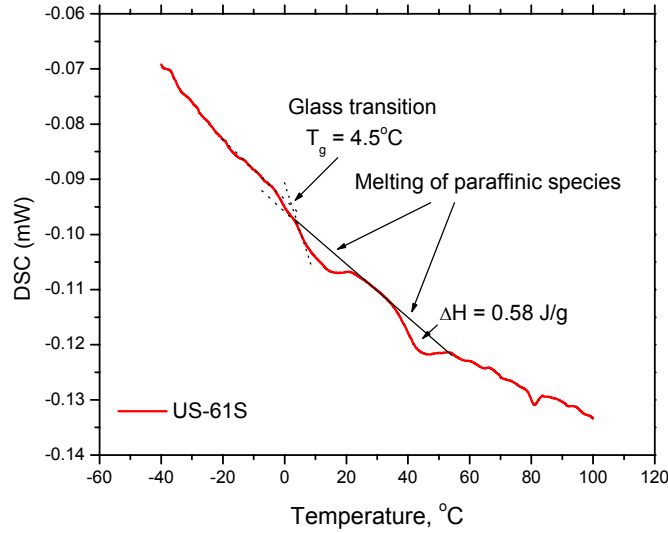


Figure 4-5.
Glass transition and paraffinic crystallinity of US-61S binder

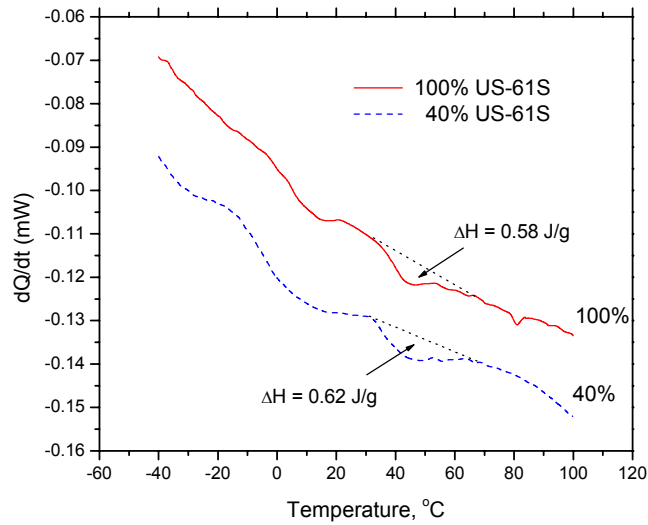


Figure 4-6.
Paraffinic crystallinity of US-61S binder and of the blend containing 40 percent US-61S binder and 60 percent PMAC

The thermal transitions of the asphalt binders are summarized in Table 4-1. Note the impact of blending on the extent of crystallinity. The presence of polymer in the virgin PMAC lowered the extent of crystallinity. Conversely, the addition of age hardened asphalt components raised the extent of crystallinity in the resultant blend five fold relative to that of virgin PMAC. The increases in crystallinity will increase the tendency of these blends to undergo low temperature cracking and will reduce their fatigue resistance.

Table 4-1. Thermal transitions of asphalt binders

SAMPLE	Tg °C	Tm1 °C	Tm2 °C	$\Delta H_{\text{fusion}}^*$ mJ/mg
AC-30	**	54	67	0.33
PMAC	**	55	67	0.16
PAV-PMAC	-11.0	56.3	68	0.16
US61C Binder	4.5	34	81	0.58
20% US61	-0.5	31	60	0.77
40% US61	-3.1	34	60	0.62
60% US61	3.8	30	60	0.56

*Total area of crystalline transitions

**Below -20

CHAPTER 5[‡]

RHEOLOGY AND MECHANICAL ANALYSIS

Original (Tank) PMAC

The PAC-40HG sample was subjected to standard short-term and long-term aging procedures and then characterized according to the SHRP protocol. The results are presented in Tables 5-1, 5-2 and 5-3. The data were consistent with those reported by the industrial provider of asphalt samples.

PMAC and Aged PMAC Blends

The feasibility of using recycled PMAC was studied by blending the virgin PMAC with lab-aged (PAV-aged) PMAC at different percentage (0, 20, 40, 60 percent) at 100 to 135°C. The lab-aged PMAC was consistently stiffer than the virgin asphalt as would be expected from extended field aging.

Typical LADOTD high volume mixtures were made containing as a binder PAC-40 or the blends of PAC-40 with PAV aged PAC-40 as shown above. After applying a short and a long term aging to the designed mix to simulate field conditions, the binder was extracted from the mixes and its rheological characteristics were compared with those from the binder study.

The SHRP protocol was employed for performing the measurements. The testing parameters were the following: measurement type - high temperature range; target temperature - different values; strain amplitude - 12.00 percent; plate diameter - 25.0 mm; plate gap - 1,000 μm (1.0 mm); and equilibration time - 3.0 minutes. Figure 5-1 shows the results for a binder

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extracted from an aged mixture containing PAC-40 with 0% (viz., the reference material for the mixtures containing blends of aged and non-aged PAC-40).

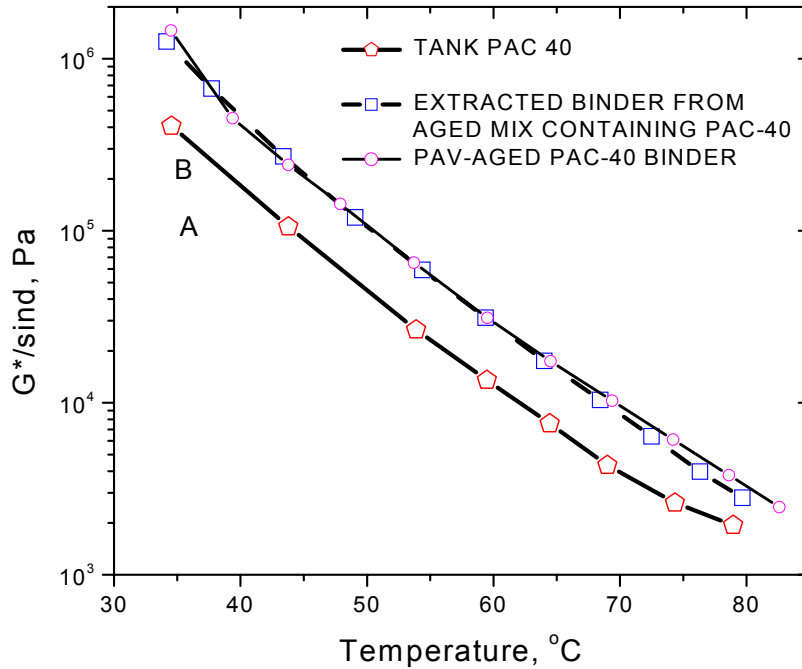


Figure 5-1.

Relative stiffness of the PAC-40 binder, of the PAV-aged PAC-40 binder and of the material extracted from a long term aged mixture containing PAC-40 with 0% pre-aged PAC-40 as expressed by the $G^*/\sin\delta$ parameter.

Perusing this plot, it can be seen that the stiffness of the extracted binder, as expressed by the SHRP $G^*/\sin\delta$ parameter, is above the stiffness of the PAC-40 and well above the minimum requirement of 1,000 Pa for temperatures up to 90°C. At the same time, there is practically no difference between the stiffness of the binder which was aged while in the mix and subsequently extracted and the stiffness of the PAV-aged PAC-40 binder. Comparing the value of $\sin\delta$ at higher temperatures (Figure 5-2), the observation that the elastic character of the

binder, reflected by $\sin\delta < 1.0$, is enhanced after aging. Table 5-1 lists the storage modulus G' at 80C.

Table 5-1. Elastic character of binders at high temperatures as reflected by the value of the storage modulus $G' = G^* \cos\delta$ at 80°C.

Binder	δ (°)	G'
Tank AC-30	90	0
Tank PAC-40	79.02	0.19G*
PAV-Aged PAC-40	72.50	0.30G*
Extracted Mix-Aged PAC-40	71.26	0.32G*

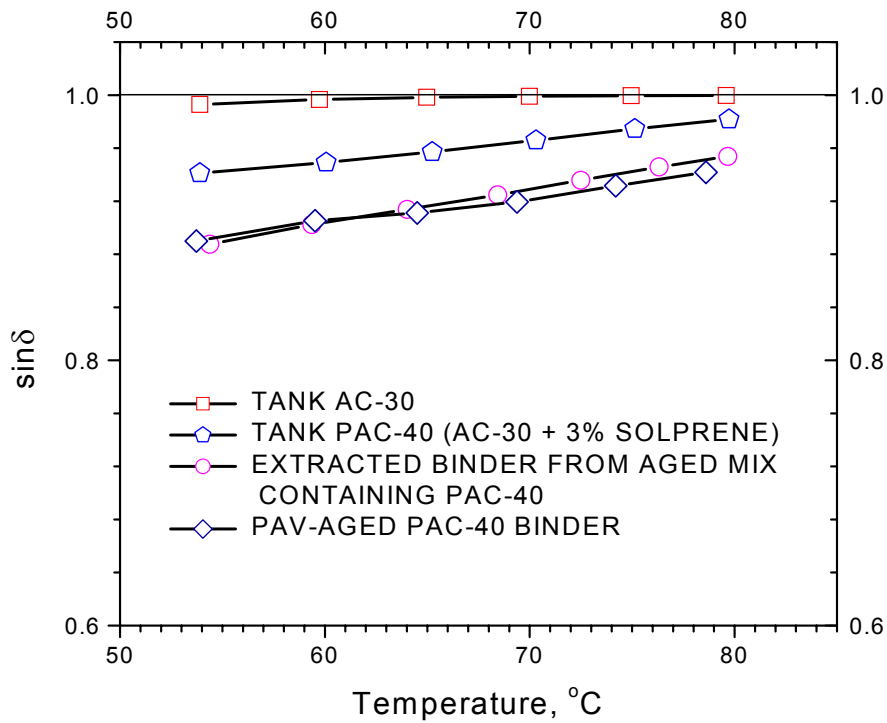


Figure 5-2. Variation of $\sin\delta$ with temperature of the tank AC-30, tank PAC-40, PAV-aged PAC-40 and the binder extracted from the long-term aged mix containing PAC-40.

As expected, the elasticity of the binding system was enhanced by aging, perhaps by creating a more compatible network system. Therefore blending with virgin asphalt cement can produce PAC-40 type binders with qualifying stiffness values for a rather large range of higher temperatures.

Table 5-2: Original AC-30 binder rheological characterization

Material		AC-30	
Weight Loss, %	After TFOT	<1%	
BBR, after PAV, -16°C	Stiffness (MPa)	173	
	Slope (m)	0.348	
DSR test	G*/sinδ @64°C, pa	Original	1448
		TFOT	4295
		PAV	12893
	G*/sinδ @76°C, pa	Original	338
		TFOT	832
		PAV	2491
	G*/sinδ =1000pa@T°C	Original	66.8
		TFOT	72.2
		PAV	83.1

Table 5-3: Rigidity test results

Parameter	AC-30	PMAC-40HG
Original		
1. Work, Nm (lbm)	0.04 (0.48)	18.65 (165.35)
2. Maximum load, N (lb)(F ₂)	70.02 (15.77)	134.58 (30.31)
3. Load at 100% elongation, N (lb)(F ₁)	-	61.01 (13.74)
4. Elongation at maximum load, m (in)	0.0025 (0.0984)	0.0123 (0.484)
5. F ₁ /F ₂		0.45
TFOT Aged		
6. Work, Nm (lbm)	11.2 (99.28)	15.56 (146.86)
7. Maximum load, N (lb)(F ₂)	163.17 (36.75)	134.27 (30.24)
8. Load at 100% elongation, N (lb)(F ₁)	-	53.32 (12.01)
9. Elongation at maximum load, m (in)	0.008 (0.315)	0.0085 (0.3346)
10. F ₁ /F ₂	-	0.40
PAV Aged		
11. Work, Nm (lbm)	0.16 (1.4)	15.36 (136.24)
12. Maximum load, N (lb)(F ₂)	103.76 (23.37)	127.83 (28.79)
13. Load at 100% elongation, N (lb)(F ₁)	-	52.35 (11.79)
14. Elongation at maximum load, m (in)	0.0027 (0.1063)	0.0112 (0.4396)
15. F ₁ /F ₂	-	0.41

The relative stiffness of the blends, expressed as $G^*/\sin\delta$ at selected qualification temperatures is summarized in Table 5-4.

Based on the specification of a minimum $G^*/\sin\delta = 1000$ Pa, addition of aged PMAC raises the minimum temperature for qualification with regards to stiffness. The consistency of the blends was measured by rotational viscosity at 135°C. Although an increase in viscosity is noted (Table 5-5), neither the blends nor the pure PAV aged PMAC exceeded the practical limit of 3.0 Pa.s for high temperature viscosity. The presence of the polymer additive exerts a moderating influence on the age hardening of the asphalt matrix. Therefore, the preliminary results indicate that recycling of PMAC's should be feasible.

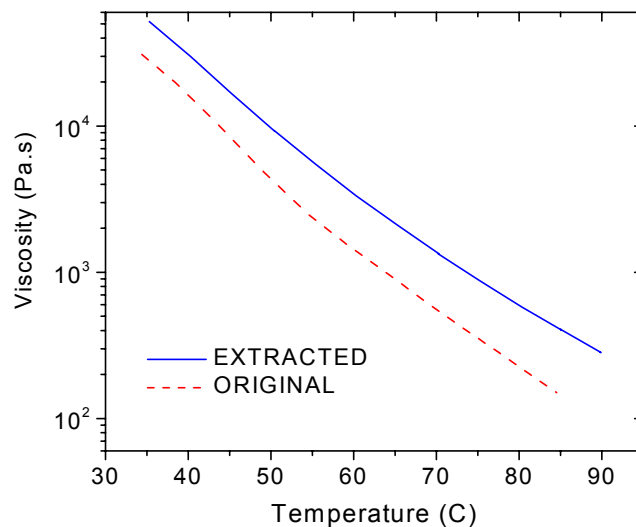


Figure 5-3.
Comparison between viscosities of 60%PAV aged PAC-40 asphalt cement and the material extracted from a mixture prepared with 60%PAV aged PAC-40 asphalt cement.

It has been found that the material extracted from the mixture had a much higher viscosity (Figure 5-3) and a stronger viscoelastic character, as indicated by lower values of the sine of the loss angle δ (Figure 5-4). The extracted material should be similar to a TFOT aged

60%PAV aged PAC-40. It seems that a more drastic aging occurred during the preparation of the mixture than in the TFOT oven (Table 5-7).

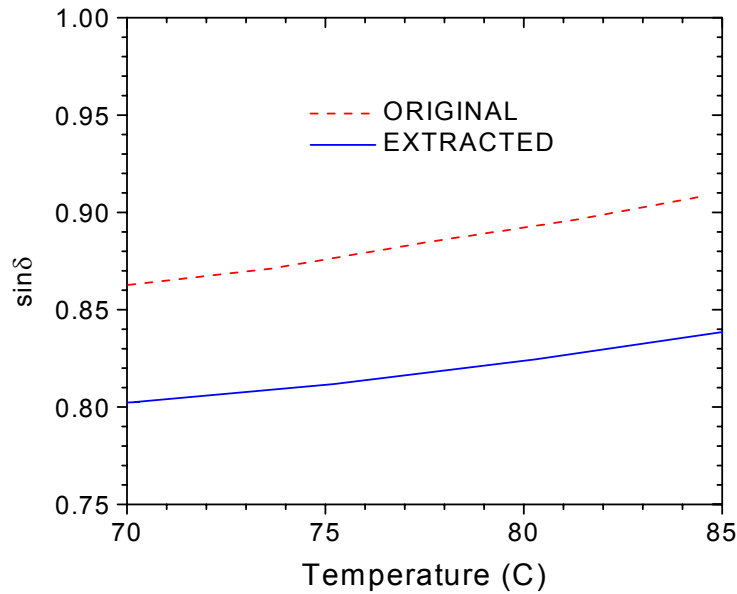


Figure 5-4.

Sin of the lost angle δ as an indication of the viscoelastic character of 60% PAV aged PAC-40 asphalt cement and the material extracted from a mixture prepared with 60%PAV aged PAC-40 asphalt cement

All blends have been PAV aged and their stiffness was determined by measuring the low-temperature creep response using a bending beam rheometer (Cannon TEBBR). The Superpave SHRP protocol was observed for these measurements. The data, which were collected at six loading times (8, 15, 30, 60, 120 and 240 sec) for a load on the beam of 100 ± 5 g, allowed the calculation of the creep stiffness, $S(t)$, and the creep rate of the sample under load, m , as the absolute value of the slope of the log stiffness versus log time curve. The results are shown in Figure 5-6.

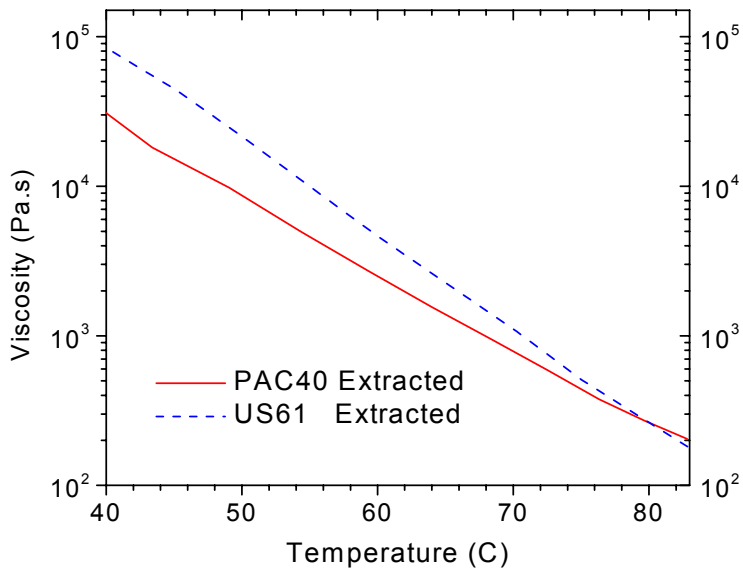


Figure 5-5.
Comparison between the dynamic viscosity of the binder extracted from US61 Hwy (Livingston Parish) and that of PAC-40.

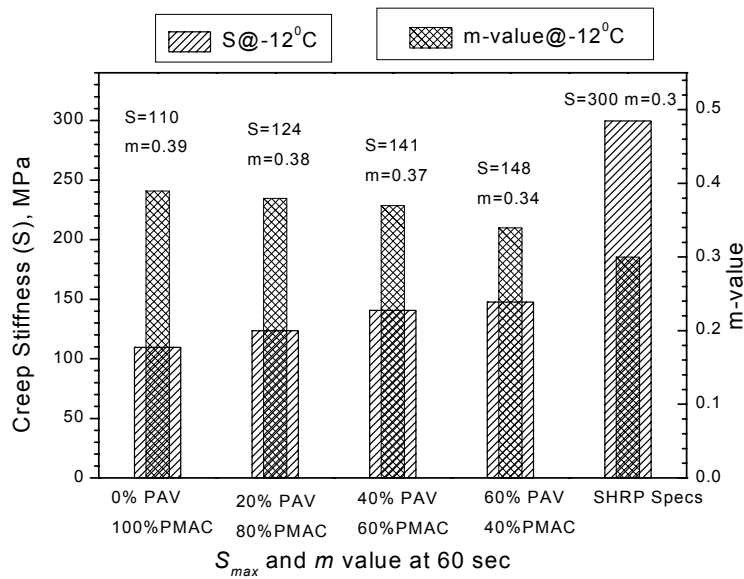


Figure 5-6.
Creep and creep stiffness determined at -12°C for PAV aged PMAC blends containing *a priori* PAV aged PMAC material

Table 5-4. Rheological data for blends of PMAC with PAV-aged PMAC

Material (% PAV PMAC)	$G^*/\sin\delta@64^\circ\text{C}$ kPa	$G^*/\sin\delta@76^\circ\text{C}$ kPa	$G^*/\sin\delta = 1.00$ kPa @T°C
0%	3.615	1.029	76.1
20%	4.400	1.244	78.4
40%	5.250	1.488	79.9
60%	8.263	2.148	82.8
100%	18.927	5.135	92.8

Table 5-5. Viscosity of blends of PMAC with PAV-aged PMAC

Material (% PAV-aged PMAC)	Viscosity @ 135°C (Pa.s)
0%	1.125
20%	1.340
40%	1.547
60%	1.832
100%	2.580

As expected, the stiffness increased with the content of the aged material, remaining, however, in the lower half of the accepted maximum value. Accordingly, the creep rate experienced a low decrease, remaining much above the minimum qualifying value

These properties of the extracted material will determine the in-field behavior of the asphalt binder and not the characteristics of the parent asphalt cement (i.e., pristine material).

PMAC and Field-Aged PMAC Blends

To establish the feasibility of blending recycled US61 binder with virgin PMAC, blends of PMAC with various percentages of US61 binder were made at 100 to 135°C. Table 5-6 presents test results of binder rheology at selected qualification temperatures. As shown below, the US61 binder was consistently stiffer than the virgin asphalt as would be expected from extended field aging.

Table 5-6: Rheological data for blends of PMAC with US61S

Test	Property	Test results				PG Criteria
		0% US61S	20% US61S	40% US61S	60% US61S	
Original Binder						
Dynamic Shear Rheometry (kPa)	G*/sin δ	@ 70°C	@ 70°C	@ 70°C	@ 70°C	1.0 kPa, Min
		1.782	42.3	160	187	
		@ 76°C	@ 76°C	@ 76°C	@ 76°C	
		1.029	23.8	94.8	99.7	
		@ 82°C	@ 82°C	@ 82°C	@ 82°C	
		0.55	13.6	54.4	53.4	
PAV Aged Binder						
Dynamic Shear Rheometry (kPa)	G* sin δ	@28°C	@25°C	@25°C	@25°C	5000 kPa, Max.
		1036.3	5229.5	6911.3	8889.1	
		@ 31°C	@28°C	@28°C	@28°C	
		707.4	3716.5	5360.9	7064.9	
		@ 31°C	@ 31°C	@ 31°C	@ 31°C	
		2657.5	3917.2	5518.8		
Bending Beam Rheometry (-12°C)	Stiffness	110	219	246	249	300 MPa, Max.
Bending Beam Rheometry (-12°C)	M value	0.39	0.271	0.246	0.229	0.300, Min.

Table 5-7. Comparison between G*/sinδ parameters of TFOT aged 60%PAV aged PAC-40 asphalt cement and of the material extracted from a mixture prepared with 60%PAV aged PAC-40 asphalt cement.

Material (60% PAV PMAC)	G*/sinδ@76°C Pa	G*/sinδ@82°C Pa
TFOT	3,652	1,984
*E60%	11,633	6,910

*Material extracted from a mixture prepared with 60%PAV PMAC

In addition, the high temperature stiffness factor, or the rutting factor of the blends, expressed as G*/sinδ at selected high temperatures increased significantly after the addition of

only 20 percent US61 binder to PMAC: the $G^*/\sin\delta$ value jumped from 1.03 kPa to 23.8 kPa. The higher the $G^*/\sin\delta$ value, the better the binder resists permanent deformation.

On the other hand, the fatigue cracking factor, termed as $G^*\sin\delta$ at intermediate temperatures also increased rapidly because of the inclusion of US61 binder. It is noted that all $G^*\sin\delta$ values of various of US61 binder contents (20, 40 and 60 percent) at 25°C exceed the maximum Superpave specification value of 5000 kPa, which indicates high fatigue cracking tendency for the binders. Moreover, BBR test result showed that the addition of US61 binder would also increase the thermal cracking potential.

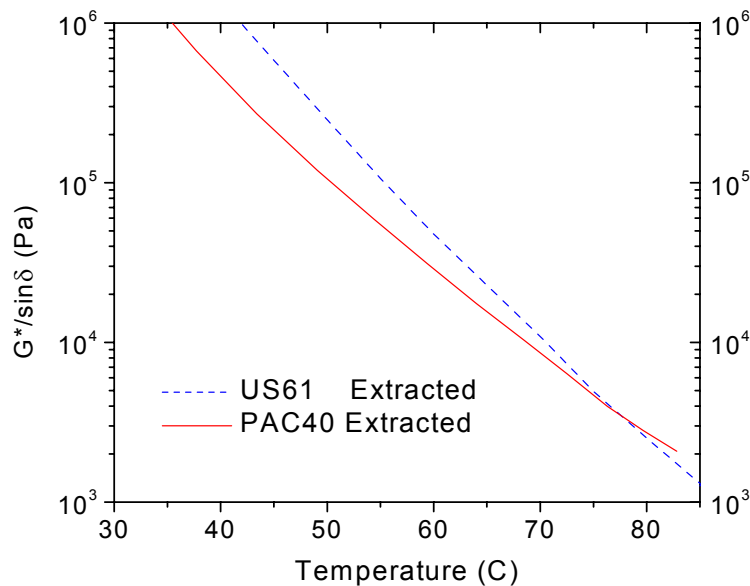


Figure 5-7. Comparison between the stiffness parameter $G^*/\sin\delta$ of the binder extracted from US61 Hwy (Livingston Parish) and that of PAC-40.

To initiate an answer to the question "Will the polymer additives degrade or harden during long term exposure to field conditions and thus no longer contribute to the binder properties? ", an in-road aged binder was extracted and compared with the PAC-40 asphalt

cement used throughout the present investigation. Figure 5-5 compares the viscosity of the binder extracted from US61 Hwy (Livingston Parish) with that of PAC-40. As expected, the in-road-aged material is more viscous at the lower end of temperatures tested, but the difference vanishes at higher temperatures of interest, viz., 75-85°C. A similar trend was observed between the variation with temperature of the stiffness parameter $G^*/\sin\delta$ of these two materials (Figure 5-7).

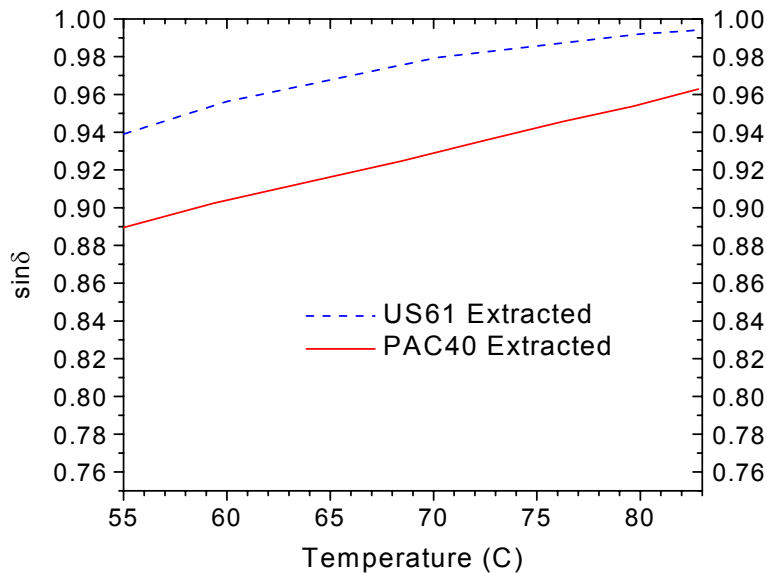


Figure 5-8.
Comparison at higher temperatures between $\sin\delta$ of the binder extracted from US61 Hwy (Livingston Parish) and that of PAC-40

Incorrect conclusions might be drawn if the viscoelastic character described by $\sin\delta$ is not analyzed at higher temperatures. One may notice that the in-road aged material has a clear tendency for a Newtonian flow ($\sin\delta = 1.0$) at high temperatures, similar to polymer-free tank asphalt cement (Figure 5-2), while PAC40 (Figure 5-8) or its aged counterparts (e.g., Figures 5-2 and Figure 5-4) exhibit at the same temperatures a strong viscoelastic character. These

preliminary data might be an indication for a very limited contribution of the polymer to the behavior at higher temperatures of the in-road-aged binder.

Forced Ductility

All of the binders containing field-aged asphalts (20, 40, and 60 percent US-61C in PMAC) were too brittle and failed this test at the required temperature, viz., 4°C. They all exhibited a very low ductility (less than 30 percent) and a high load at failure (varying from 180 to 260 lb with the increasing amount of field aged material in the blend). The lowest temperature at which US-61C passed the test was 15°C (Figure 5-9).

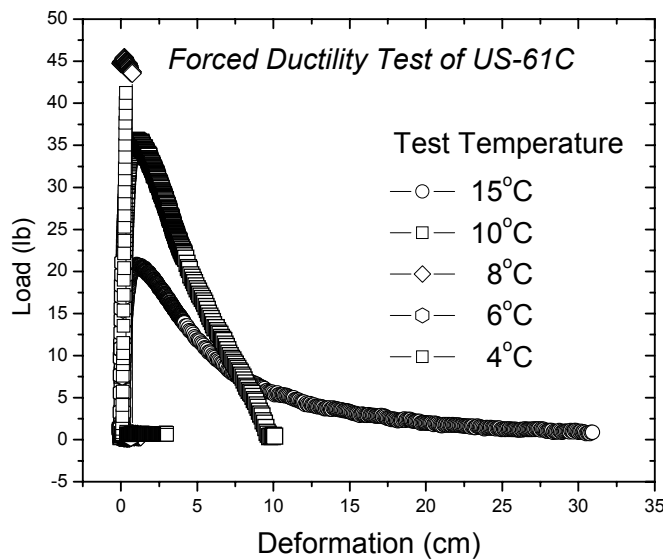


Figure 5-9.
Forced ductility data at different temperatures for US-61C binder

Forced ductility data confirmed thus the positive glass transition temperature of field-aged binders observed by DSC measurements (Figure 4-5).

Critical Gel Transition Temperature

In addition to the polar chemical functional groups formed on oxidation, asphalt properties can also be significantly altered by molecular structuring, sometime called steric hardening. This potentially reversible phenomenon may also be a major factor contributing to pavement embrittlement.²⁷ While difficult to quantify in asphalt pavement mixtures, it is highly dependent on temperature. Early on the road of determination of the rheological properties of asphalts in relation to durability and pavement performance, Sisko and Brunstrum pointed out that aging produces changes in consistency that appeared to be due to the development of a gel structure.⁶⁵

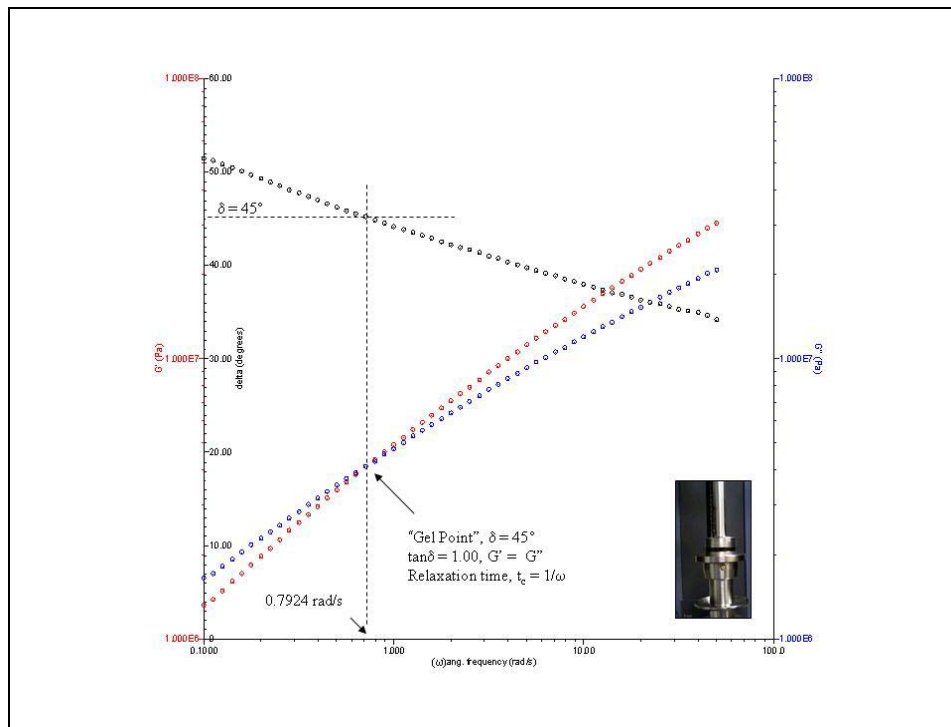


Figure 5-10.

Plot of G' and G'' vs frequency applied to the determination of the cross-over temperature of the AC 64-22 aged without water for 30 hrs (1.5xPAV)

Heteroatoms introduced by aging may have formed secondary valence bonds that were involved in the gel. Evidence for the gel structure came from a number of observations: the aged asphalt did not flow back into a crater cut into its surface, the penetration-softening point relation changed, the viscosity increased greatly with small increase in molecular weight, the WLF constants of time-temperature superposition relationship⁴⁹ changed, and large changes of viscosity occurred without a significant change in temperature.

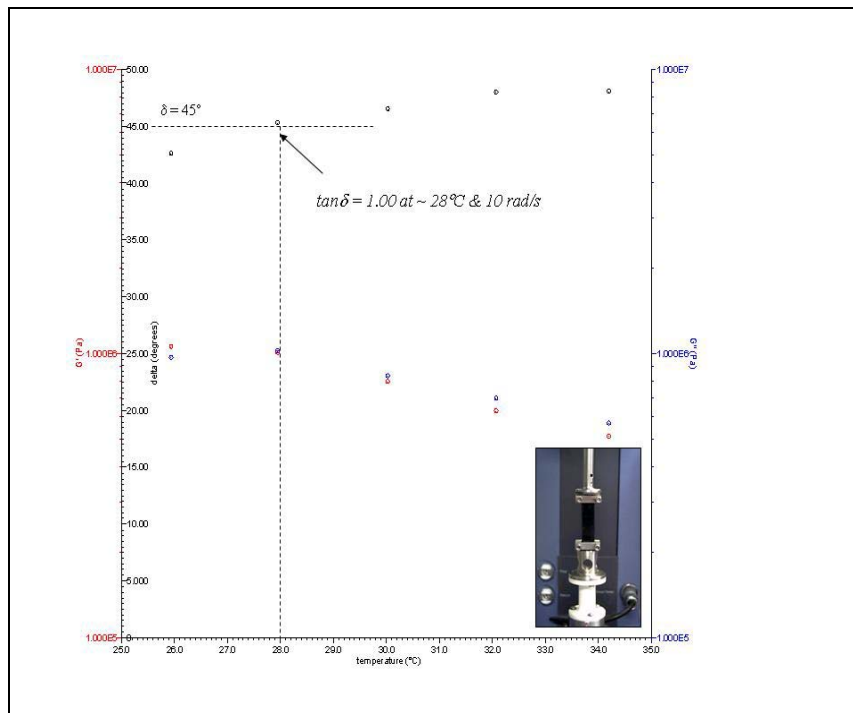


Figure 5-11.

Plot of G' and G'' applied to the determination of the cross-over temperature of the PMAC 77-22 aged without water for 20 hrs (1.0xPAV)

By adding polymers, such as cross-linkable rubbers, the gel character of asphalt cements is enhanced. The three dimensional network resist deformation and recover the initial shape at temperatures at which the storage modulus (G') is superior to the modulus describing the viscous character of the asphalt, i.e., the loss modulus (G''). The effectiveness of the

network diminishes rapidly above the cross-over temperature at which these two moduli become equal ($G' = G''$ at $\delta = 45^\circ$ for which $\tan\delta = 1$).

This cross-over temperature (to be called critical temperature, T_c , in the following) is proposed in the present work to discern the changes in rheological characteristics of polymer modified asphalts brought about by aging. Applying a special high frequency torsional rheometer to study the impact of long term aging of asphalt joint materials, Swiss scientists proposed the unitary value of $\tan\delta$ as a distinctive threshold point for analyzing aging of bituminous binders.⁶⁶

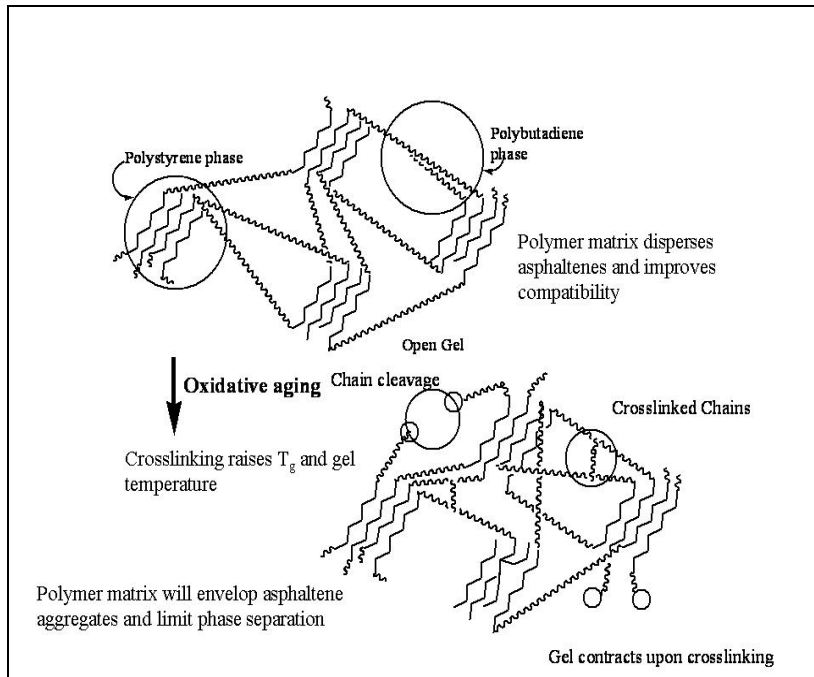


Figure 5-12.
Oxidative aging of the SBS polymer matrix in PMAC asphalts

Figures 5-10 and 5-11 exemplify the determination of T_c for laboratory aged AC 64-22 and PMAC binders, respectively. As expected, the cross-over temperature increased after adding polymer to the asphalt cement (Table 5-8).

When SBS are used as an asphalt additive, the oxidative aging changes the polymeric matrix towards an open gel structure still capable of stabilizing asphaltene/maltene emulsion (Figure 5-12).

The cross-over temperature depends, however, on the frequency at which the test is conducted: the higher the frequency, the higher the temperature. Therefore for each temperature a relaxation time can be determined, corresponding to the frequency at which the moduli are the same: the higher the temperature, the shorter the time. An example is shown in Figure 5-13 which describes the variation of $\tan\delta$ of the PAV dry-aged PMAC sample.

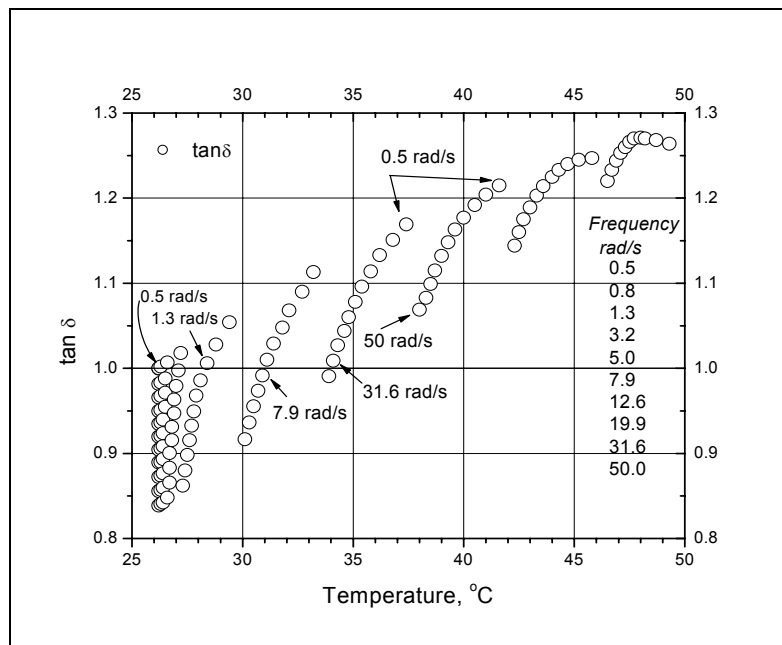


Figure 5-13.

Variation of $\tan\delta$ with temperature for dry-aged 1.0xPAV PMAC sample.

In order to compare the results all determinations were made using a frequency of 10rad/s. The results are presented in Figure 5-14. Extremely high critical temperatures have been recorded after only three-four full PAV aging cycles. Surprisingly, wet-aging produced

much softer materials, with a T_c of samples aged for 70 hrs equivalent to that of dry-PAV samples aged for only 30-40 hrs.

Table 5-8. Critical temperatures T_c ($\tan\delta = 1$, $G' = G''$) of aged asphalt samples determined at a frequency of 10 rad/s

Asphalt Sample	Aging Time	T_c Dry Aged °C	T_c Wet Aged °C	T_c Road Aged °C
AC 64-22	Unaged	8.2		
PMAC 76-22	Unaged	9.5		
PMAC 0.5xPAV	10 hrs	23.8	20.3	
PMAC 1.0xPAV	20 hrs	30.6	22.1	
PMAC 1.5xPAV	30 hrs	42.0	36.0	
I-55 Extract	3 yrs			21.0
I-55 Extract	5 yrs			27.3
I-55 Extract	7 yrs			29.4

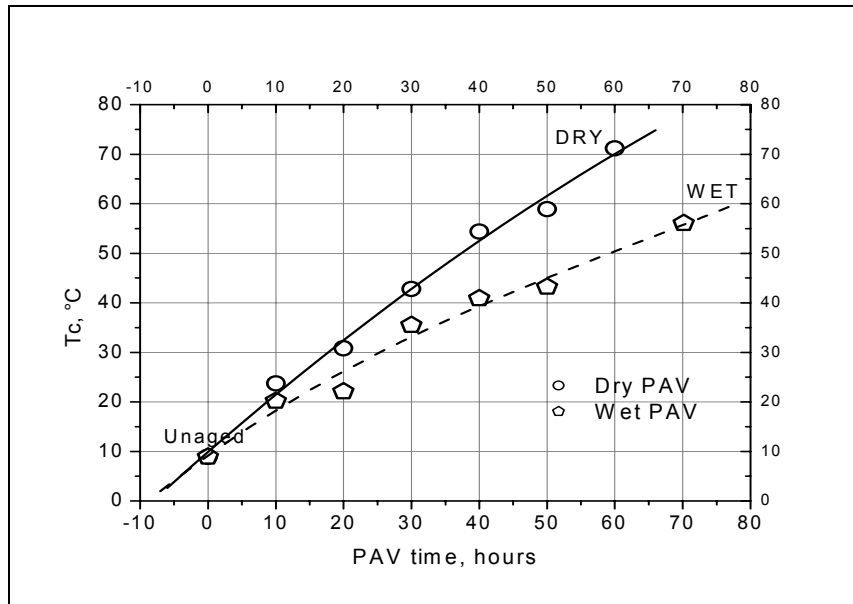


Figure 5-14.

Variation of critical temperature of multiple PAV dry-aged and wet-aged PMAC samples. The combined effects of oxidative aging of SBS and asphalt components, i.e., crosslinking of polymer and aggregation of asphaltenes, lead to higher gel points (T_c).

There is a rather short temperature domain, less than 10°C, for which $\tan\delta = 1$ ($G' = G''$), with the lower end concentrating to low frequency.

Critical temperatures of PMAC laboratory aged samples are compared with that of asphalt samples extracted from I-55 aged pavements in Table 5-8. Perusing data listed in this table, one might conclude above, the oxidation process is controlled at given temperature by the reactivity of the binder and the rate of diffusion of oxygen into the binder. As the viscosity of asphalt increases, the coefficient of diffusion of oxygen decreases. The coefficient of diffusion was found also dependent on the concentration of chemically bound oxygen, viz., as the later increases the coefficient decreases.⁶⁷ The concentration of chemically bound oxygen was found to be higher in asphalt samples aged in presence of water both in this work and in other investigations.³² Water might therefore moderate the aging process towards a more open gel structure which, at its turn, translates in a “softer” material with a corresponding lower T_c . The chemistry of the water effect on PMAC aging is under investigation.



Figure 5-15.
Cores taken from LA 3234 Hwy

The diagram developed in Figure 5-14 can be calibrated with data presented In Table 5-8 for field-aged I-55 Hwy samples. The cross-over temperature can be used then as a criterion to build a nomogram for assessing the aging of SBS PMAC binders (other polymeric additives might behave differently on aging because of the lack of double bonds). that the maximum critical temperature exhibited by the sample aged for 7 years is more similar to that of the PMAC sample aged for 20 hrs in absence of water (one dry PAV cycle), while shorter periods of aging on the road (3-5 years) produced samples with a cross-over temperature somewhat closer to that of PMAC samples aged in a wet atmosphere for 10-20 hrs.

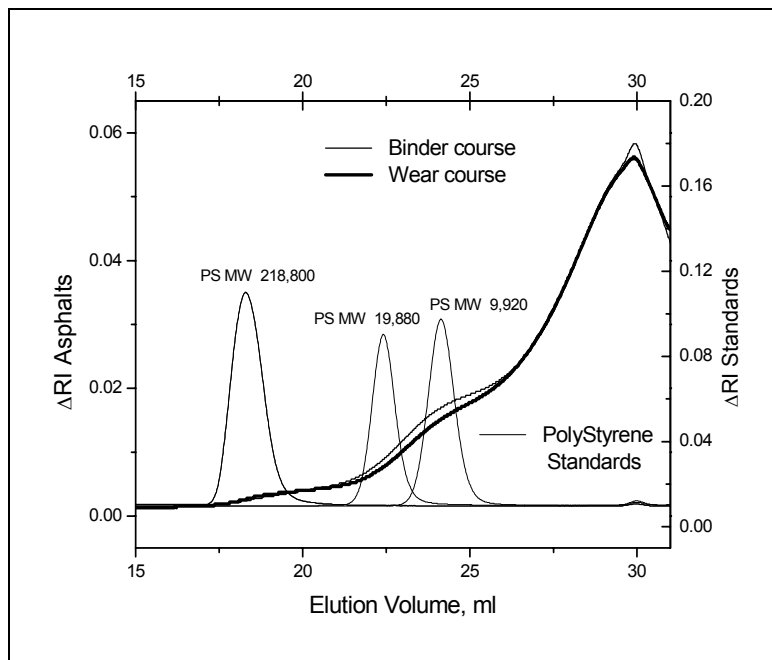


Figure 5-16.
GPC traces of asphalts extracted from LA 3234 Hwy paving samples

The cross-over temperature criterion was applied for checking the binder characteristics extracted from a distressed LA 3234 Hwy with three years of service. SBS was also the polymer additive used by contractor for the preparation of the PMAC composition. The cores

from which the binder was extracted are shown in Figure 5-15. The presence of the polymer was clearly identified by GPC measurements which produced diagrams similar to that of I-55 Hwy binder extracts presented above. GPC chromatograms of LA 3234 Hwy binder extracts are shown in Figure 5-16. Polystyrene standards mark the domain of interest of polymeric and asphaltene species. The content of LMS suggested that the aging degree of the wear course was less advanced than that of the binder course (compare MW traces around 10^5 Daltons).

Rheological measurements at 10 rad/s resulted in a crossover T_c of 25.2°C for the wear course and 26.4°C for the binder course. The wear course extract had also a lower complex viscosity at 25°C (4.4×10^5 Pa.s) than the binder course (5.5×10^5 Pa.s), in agreement with GPC and T_c data. Critical temperatures of 25 to 26°C are experienced for pavements 3-5 yrs old (dry aging) or 5+ years for wet conditions. The fact that the data for the wear course point to a less advanced degree of aging than that of the binder might be related to the moderation effect of water. At any rate, the T_c values listed above (less than 30°C) do not suggest that the LA 3234 Hwy extracts are over aged binders and other reasons should be considered for the rather rapid degradation of this road.

CHAPTER 6 CONCLUSIONS

Overview/Summary

Polymer modified asphalt cements are complex compositions containing molecular species that answer differently to the orchestrated actions of aging agents. The aging intensity of elastic pavements is dictated among other factors (e.g., intensity of the traffic, climate) by the pavement depth; superficial layers are prone to be degraded drastically as compared to the same compositions situated just inches below. This was shown in the present study by GPC analysis of the asphalt extracted from US 61 road pavement sampled by abrading the road surface (no polymer detected) or as a deep core (aged polymer detected). While the depreciation of asphalted roads is initiated by micro cracks developed on the stiff surface, their in-depth propagation is blocked if the asphalt cement holding together the paving mixture has a balanced viscoelastic characteristic. The elastic characteristic of the asphalt cement is enhanced tremendously by SBS block copolymer over a large temperature domain. However, the butadiene blocks are the first to be sacrificed by oxidative aging of asphalt cements, raising their glass transition, T_g , and correspondingly their stiffness in temperature domains too high even for mild climates, such as that of Louisiana and other Gulf states.

While the SHRP methodology was observed for rheological characterization of asphalt cements throughout this investigation, it became evident that the complexity of aging polymer modified compositions can not be treated according to standard methods developed for paving compositions free of polymeric additives. Therefore a new rheological parameter has been considered for analysis of data collected in the present study of advanced aging of elastomeric asphalt compositions, viz., the point at which, by raising the temperature, the elastic component

of the modulus of rigidity of the material decreased to the same value as that of the viscous component. This equilibrium is reflected by the unitary value of $\tan\delta$. For higher temperatures the viscous component takes over the whole viscoelastic behavior of the material. It has been shown that this cross-over temperature at which $\tan\delta=1$ (determined at the standard SHRP frequency of 10 rad/s) increased dramatically as the polymer modified asphalt cement was aged in laboratory; it was also dependent on the aging conditions: dry or wet. The presence of water played a major role in the chemistry of aging processes; it promoted a sharp increase of carbonyl and acid functionalities in asphalt composition. At the same time, water seemed to have a retarding effect on asphalt hardening: all critical temperatures at which $\tan\delta=1$ were lower when water was present in the aging device. A confirmation to this moderation effect of water on aging of asphalt pavements was observed when the data for asphalt cement sampled from interstate I-55 after 3, 5 and 7 years on the road were compared with data of similar polymer asphalt compositions aged in laboratory in dry and wet conditions. The moderation effect of water on asphalt aging was also observed by analyzing materials sampled from LA Hwy 3234, pointing to a practical use of this simple rheological parameter: nomograms can be built for aging of polymer modified asphalt cements and used for assessing of aging of similar road pavements. A comparison to nomogram data can indicate a premature distress or can show that the pavement did not yet reach its “retirement” age and can be still used to its full capacity.

Rheological Investigations

The asphalt architecture has been simulated with that of a gel. The cross-over temperature at which G'' equals G' , as temperature increases, was considered as critical temperature (T_c), and chosen as a criterion to assess the advancement of hardening (aging). We observed that the

critical temperature is dependent on frequency, therefore to compare the properties of differing asphalt samples, data was collected at a frequency of 10 rad/s.

Initially the SBS copolymer additive helped to disperse the asphaltenes. Oxidative cleavage of allylic bonds shortened the B blocks and encouraged formation of an open gel structure. Upon aging, the copolymer crosslinked and contracted around the asphaltene aggregates. The combination of these effects with aggregation of asphaltenes led to an increase of the PMAC critical temperature. Water had a retarding effect on hardening. Critical temperatures of asphalts aged in presence of water were lower than those of dry-aged PAV samples. The chemistry of this effect is under investigation.

Processes Occurring During Laboratory Aging of PMAC Samples

Aging properties of the PAV-aged PMAC and US61 binders were characterized by an FTIR analysis and a calibration curve based on benzoic acid concentrations used to estimate the carbonyl content of aged asphalt binders. The oxidization of each asphalt binder was identified by a set of peaks centering around 1700 cm^{-1} , which correspond to carbonyl absorptions of oxidized species, in the infrared spectra. The results showed that the US61 binder samples from the road surface exhibited a higher extent of oxidation than the PAV-aged PMAC; the greater the percentage of US61 binder mixed with virgin PMAC binder, the higher the concentration of oxidized species was detected.

Using multiple PAV treatments we found that the concentration of carboxylic acid groups increased with the aging time. The production of carboxylic acid was higher when the aging operations were carried out in the presence of water. We believe that this is due to increased likelihood of free radicals reacting with water molecules rather than another

hydrocarbon chain, along with the fact that water not only brings more oxygen to the reaction media in its own structure, but it also incorporates dissolved atmospheric oxygen, facilitating the formation of aldehyde groups and their further oxidation to carboxylic acid.

Generation of acid carboxylic groups may improve the adhesion to aggregates from asphalt pavement. At the same time, the acidic polar groups could lead to aggregation of asphaltene components from base asphalt cement. Aging leads to a drastic reduction of molecular mass of SBS species and an increase in the content of low molecular weight asphalt components.

Field Data Evaluation

This brittleness of binder can be related to mobility of asphalt species as reflected by the glass transition. The higher the glass transition temperature, the more brittle the binder at low temperatures. The glass transition temperature of US61 binder was found higher than that of PAV aged PMAC and correspondingly. The higher the US61 content in the blends of US61 and PMAC, the higher the glass transition the binder has.

The increase in glass transitions and increases in crystallinity will increase the tendency of these blends to undergo low temperature cracking and will reduce their fatigue resistance. Critical temperature of the field 3 year old I-55 paving sample correlated better with the laboratory wet 0.5xPAV aged PMAC sample. Critical temperature of the field 5 year old I-55 sample was intermediate between T_c of the dry 0.5xPAV and that of the dry 1.0xPAV laboratory aged PMAC samples. Critical temperature of the field 7 year old I-55 sample correlated better with the laboratory dry 1.0xPAV aged PMAC sample. By calibrating the

laboratory aging results with field data a nomogram can be obtained for assessing the aging of SBS PMAC binders.

This type of correlation was successfully used to determine if a binder extracted from a damaged road pavement was excessively aged after three years of service. The correlation will work equally well with older pavements, allowing us to analyze and quantify the degree of aging and recyclability of a damaged asphalt pavements.

CHAPTER 7 FUTURE WORK

A better understanding of the mechanism by which the presence of water affects the oxidation/aging of polymer modified asphalt cements would be part of the future work that needs to be done on this project. A rotary cylinder type of aging instrument will be used in order to permit a greater variation of the aging conditions (such as oxygen content, water content, time, and temperature of the process). The ability to obtain and analyze samples at various times during the lab aging process is key to understanding how aging occurs and what are its steps and evolution in time. FTIR measurements along with titration methods and GPS data will help follow the chemical changes that occur during aging. Rheological measurements will keep track of the performance modifications induced by the aging process.

Using the information gathered during the above mentioned investigation, a new generation of lab aging techniques and instruments will need to be developed. These new instruments and laboratory aging techniques will better duplicate the field aging conditions and reflect a more accurate image of the transformations and stresses that occur during the service life of the asphalt pavements. The presence of the polymer modifier and its own oxidation mechanism will need to be accounted for in order for these new techniques to effectively simulate the field aging process. Ideally the number of the instruments in use today to measure the asphalt binder's properties will be greatly reduced in the future by employing more capable rheometers with a more flexible sample size and shape.

Ultimately a new Superpave type protocol for testing and grading asphalt binders will be developed specifically for today's polymer modified asphalt cements. This new protocol should include more flexibility in choosing the aging conditions for the laboratory samples.

This will allow state and local agencies to customize the lab aging conditions so they would better match the local weather and traffic patterns.

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APENDIX: PERMISSION LETTER

From Domoff, Daniel J. <DJDomoff@4SPE.ORG>
Sent : Wednesday, October 19, 2005 2:12 PM
To : "Codrin Daranga" <cdaranga@hotmail.com>
CC : <chdaly@lsu.edu>
Subject : RE: To the Managing Editor of Society of Plastic Engineers

Dear Mr. Daranga: Permission granted. Best regards and best of luck.---Daniel J. Domoff

Daniel J. Domoff
Managing Editor
Society of Plastics Engineers
203-740-5429

-----Original Message-----

From: Codrin Daranga [<mailto:cdaranga@hotmail.com>]
Sent: Wednesday, October 19, 2005 3:05 PM
To: Domoff, Daniel J.
Cc: chdaly@lsu.edu
Subject: To the Managing Editor of Society of Plastic Engineers

Dear Mr. Daniel Domoff,

My name is Codrin Daranga and I am a graduate student in the Chemistry Department of Louisiana State University. My Research is focused on recycling of polymer modified asphalt cements, and is conducted under the supervision of Dr. Louay Mohammad, Dr. Ioan Negulescu, and Dr. William Daly. I am writing to ask your permission to reprint parts of the bellow mentioned article, published in the ANTEC conference proceedings from 2003, in my Dissertation.

Negulescu, Ioan I.; Daranga, Codrin; Wu, Zhong; Daly, William H.; Mohammad, Louay M.; Abadie, Chris. Use of recycled polymer modified asphalt binder in asphalt concrete pavements. Annual Technical Conference - Society of Plastics Engineers (2003), 61st (Vol. 3), 2835-2839.

Thank you for your time,
Sincerely, Codrin Daranga
Ph.D. Candidate
Department of Chemistry
Louisiana State University
Baton Rouge, LA 70803

VITA

Codrin Daranga graduated from the Technical University “Gh. Asachi” Iasi, Romania in 1999 with a Bachelor of Science degree in chemical engineering. At the Technical University “Gh. Asachi” Iasi, he studied technology of macromolecular compounds. His favorite topic as an undergraduate student was polymer processing, particularly tire manufacturing. Codrin was accepted at Louisiana State University in the Chemistry Department the same year he graduated with his Bachelor of Science degree. He joined Professor William H. Daly’s, and Professor Ioan Negulescu’s groups where he studied the recycling and characterization of polymer modified asphalt cements, using a variety of techniques. During this period he became familiar with the concepts of civil engineering related to asphalt design and construction, having access to the invaluable guidance of Dr. Louay N. Mohammad.