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16. Abstract

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PAV aging of the asphalt rubber blends revealed a significant difference between crumb rubber and powdered rubber additives. Simple blends of crumb rubber with asphalts ranging in grade from AC5 to AC30 exhibited phase separation during the thin film oven aging test. In contrast, blends with powdered rubber appeared to remain compatible or at least partially compatible through the PAV aging process and the blends retained the physical properties associated with the additive. The DMA data suggest that the low temperature cracking resistance of asphalt /powdered rubber blends is enhanced.

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CHARACTERIZATION OF ASPHALT CEMENTS MODIFIED WITH CRUMBED RUBBER FROM DISCARDED TIRES

FINAL REPORT

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ABSTRACT

The potential legislative requirement for incorporation of scrap rubber into asphalt blends mandated a thorough evaluation of the influence of scrap rubber additives on the physical properties and aging characteristics of rubber/asphalt blends. Blends with up to 20% ground vulcanized rubber (both crumb and 200 mesh powder particles) from recycled tires were prepared with asphalt cements of various grades (AC5 - AC30) and evaluated using DMA. Blends produced from powdered rubber particles exhibited Newtonian behavior at high temperatures; similar behavior was not observed with crumb rubber blends. The mechanical properties of asphalt-rubber blends depend upon the concentration of rubber additives, the particle dimensions, and the chemical composition of the asphalt. Some asphalts induced excessive swelling of the rubber particles, resulting in 135°C viscosities greater than SHRP recommended 3 Pa•Sec. The dynamic mechanical characteristics of all blends are discussed in terms of $G^*\sin\delta$ and G"; comparative data is presented according to the new SHRP binder specifications. Constant stress creep and creep recovery of the polymer or rubber asphalt blends proved to be a sensitive measure of the additive content.

PAV aging of the asphalt rubber blends revealed a significant difference between crumb rubber and powdered rubber additives. Simple blends of crumb rubber with asphalts ranging in grade from AC5 to AC30 exhibited phase separation during the thin film oven aging test. These blends lost all the physical property enhancement contributed by the rubber additive. In contrast, blends with powdered rubber appeared to remain compatible or at least partially compatible through the PAV aging process and the blends retained the physical properties associated with the additive. The DMA data suggest that the low temperature cracking resistance of asphalt/powdered rubber blends is enhanced.

IMPLEMENTATION STATEMENT

This study encompassed exploratory work to examine the procedures for producing rubber/asphalt blends and the potential for application of dynamic testing procedures to characterize the blends. There are some major findings which should be considered in preparing and storing asphalt/rubber blends. Blends containing greater than 10% crumb rubber are not stable and tend to separate rapidly when held at high temperatures. Further, successful implementation of dynamic testing procedures is critically dependent upon the particle size of the rubber additives.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

AC	Asphalt Cement
DMA	Dynamic Mechanical Analysis
PAV	Pressure Aging Vessel
CR	Crumb Rubber
PR	Powder Rubber
BBR	Bending Beam Rheometer
LR	Low Recovery
SR	Slow Recovery
CoPolyR	Styrene-Butadiene Random Copolymer
EPA	Environmental Protection Agency
ISTEA	Intermodal Surface Transportation Efficiency Act
FY	Fiscal Year
LSU	Louisiana State University
SBR	Styrene-Butadiene Rubber
SBS	Styrene-Butadiene-Styrene Bloc-Copolymer
PMAC	Polymer Modified Asphalt Cement
WLF	William-Landel-Ferry
SHRP	Strategic Highway Research Program
TFOT	Thin Film Oven Test
NMR	Nuclear Magnetic Resonance
ΔH_f	Fusion Enthalpic Change
DSC	Differential Scanning Calorimetry
BCR	Rubber Block Copolymer
RT	Room Temperature
Tg	Glass Transition
DMS	Dynamic Mechanical Spectrometer
RTFO	Rolling Thin Film Oven
λ	Wave Length
S(t)	Creep Stiffness
m	Creep rate under load
Pa	Pascal
s	Second
K	Kelvin
C	Celsius
Hz	Hertz
cP	centiPoise
CRAC	Crumb Rubber Asphalt Cement
PRAC	Powder Rubber Asphalt Cement
rad	Radian
G	Shear Modulus
J	Shear Compliance

INTRODUCTION

BACKGROUND

Polymer additives are not new to asphalt researchers. Polymer additives incorporated into asphalt can be classified into three categories: rubbers, thermoplastics and fibers. Rubbers may be defined as non-crystalline polymers with very low glass transition temperatures. The concept of rubberized roads is hardly a new one since the benefits of adding natural resins to paving mixtures were observed in the first half of the last century. The advent of rubberized asphalt cements (RAC) was announced in the British patents No. 10,185 (1843) and No. 10,327 (1844) describing the modification of bitumen with gutta percha or natural rubber, respectively, for the application on road surfaces. The two materials were developed contemporaneously; the first use of asphalt paving blocks is dated as 1824 [1], while the vulcanization of natural rubber was discovered in 1839 [2]. In the USA, Goodyear replaced asphalt with rubber in 1925, when the company laid of road of solid rubber paving blocks that lasted more than 25 years under heavy traffic. Perhaps the most dramatic example of enhancing asphalt with rubber was constructed in Holland. In 1936, the Dutch paved a road near Rotterdam with rubberized asphalt that endured war-time traffic of Nazi tanks and transportation vehicles without damage. However, the initial cost of early rubberized paving products was 40 to 100 percent higher than that of conventional AC paving materials.

Although current technology is oriented toward more practical goals such as utilization of scrap tires and residues from rubber manufacturing processes, it is anticipated that asphalt cements and pavement properties and coatings can be improved by the addition of crumbed, powdered or liquid elastomers. Compatibilized rubber modifies the asphalt to improve especially the low temperature ductility, elasticity and cyclic loading properties of the mixture. Additional property improvements include: adhesion and tack, durability, softening point and cold flow, impact resistance, resilience and toughness. An ample source of scrap rubber exists; the EPA has estimated that 2-3 billion tires are collected in solid waste dumps and approximately 240 million passenger and truck tires (or 350 million passenger tire equivalents) are added to the stockpile each year [3]. Only 9 million passenger tire equivalents are projected to be recycled in asphalt by the end of 1994.

To enforce the recycling of scrap tire rubber in asphalt Congress passed the Intermodal Surface Transportation Efficiency Act (ISTEA) in 1991. [4]. Section 1038(d) of ISTEA sets minimum utilization levels for the use of recycled rubber (and/or other selected reclaimed material, such as reclaimed asphalt pavement, known as RAP) beginning in 1994 (5%) and increasing by 5% each year through 1997, where it levels off at 20%. In 1994, the minimum utilization requirement in ISTEA called for states to use 5% recycled rubber as a percentage of total tons of asphalt laid in projects receiving federal-aid funding.

The federal legislation mandates the cleanup of stockpiles over a 12-year period, which equates to 160 million passenger tire equivalents or 400 million tires annually. Recycling of crumb rubber derived from scrap tires in the paving industry is therefore only a partial answer to this problem; alternate approaches to recycling the major portion of stockpiled tires must be considered. A further area impacted by incorporating crumb rubber into asphalt cements is the recyclability of these mixes [6]. If a ton of asphalt containing 20 lb (one tire) of crumb rubber cannot be recycled, a twenty pound problem has been multiplied 100 fold. Thus, implementation of the ISTEA legislation is being reconsidered.

A moratorium approved by Congress in the FY94 transportation appropriation bill delayed implementation of the requirement in ISTEA Section 1038(d) giving states one year to further study the performance, costs and environmental impact associated with hot mix asphalt pavement containing crumb rubber. A second moratorium delaying funding enforcement of Section 1038(d) until Fiscal 1996 has just been announced [5]. The moratoria were enacted at the request of 49 state transportation departments to allow time for the requirement mandating crumb rubber incorporation to be modified to allow a wider selection of rubber additives and mix designs based upon recommendations from state departments of transportation. Accordingly, a joint research effort regarding the implementation of ISTEA Section 1038 in the state of Louisiana brings together a group of specialists from the Departments of Chemistry and Chemical Engineering from LSU and the Louisiana Transportation Research Center to evaluate the application of scrap rubber modified asphalts. In addition to the incorporation of crumb and powdered rubber, this group focuses also on the use of other polymeric waste materials consuming landfill space, such as polyolefins (especially polyethylene) and ethylene-propylene rubbers as additives for asphalt cements.

TYPES OF RUBBER ADDITIVES

Natural and synthetic latexes have been used as asphalt modifiers [7,8]. Natural latex has improved chip or aggregate retention, flexibility, increased mixture cohesion or adhesivity, and reduced temperature susceptibility, resulting in a longer service life. Synthetic latexes used in asphalt include polychloroprene and styrene-butadiene rubber(SBR) [9]. Polychloroprene modified asphalts exhibited increased elasticity, improved cohesion and decreased temperature susceptibility, as compared to conventional asphalt [8]. SBR modified asphalts have improved flexibility and elastic recovery, provided better cohesion due to a greater resistance to viscous flow under stress, and showed lower temperature susceptibility than the non-modified asphalt [7,8]. Polybutadiene rubber (BR) can be crosslinked after incorporation into asphalt, initiating reactions during the mixing step that may also help prevent aging, since the most reactive sites of the asphalt are consumed during crosslinking and, therefore, cannot be oxidized. Improvements in penetration, viscosity, ductility and tensile stress were registered for AC/SBR blends. A benefit of rubber modified asphalts is that they have the strength of asphalt when unelongated, but the strength of rubber when stretched. Rubber grows stronger due to crystallization when strained, while the asphalt tensile strength decreases [7].

Styrene-butadiene-styrene block-copolymers, SBS, are also elastic but do not necessarily increase the initial stability of the asphalt. However, they are versatile since the ratio of plastic polystyrene to rubber polybutadiene blocks can be varied at will to influence the final properties of the asphalt mix [7,10]. The block-copolymers give asphalt concrete improved flexibility, improved resistance to permanent deformation, lower temperature susceptibility, and, therefore, extended service life [8,11,12]. Cass County, Michigan, has made a commitment to polymer modified asphalt concrete, PMAC, by installing 5000 tons of Sealoflex in four overlay projects in July 1993. To date the performance of the test sections has been excellent and an unexpected benefit was the speed at which the test sections could be reopened. Truck traffic passed over a section 15 minutes after it was laid and the pavement was not even dented [13].

Several commercial modified asphalts employing rubber components at 1-14 wt% relative to the asphalt binder are available [14]. DuPont introduced Neoprene Modified Asphalt (containing rubber amounts from 1.5 to 3%), right after the issue of the first patent covering a process for rubberizing bitumen by interblending rubber latex with molten bitumen [15]. This mixture was successfully applied on highways and airport runways, in the last case to avoid hydroplaning incidents. Rubber-R-Road bituminous paving additives comprise both styrene-butadiene rubber latexes and solutions of rubber at 3-5 wt% of the asphalt content as paving and sealing compounds for roads, bridges, parking decks, airport ramps and aprons. BASF Corp. also offers a line of SBR latex products under the tradename Butanol NS XXX. Styrene-butadiene block copolymers (SBS) blended with asphalt are sold under the tradename Styrelf and have proved to be very successful in the field. Combinations of SBS and a proprietary additive premixed by Ergon at 3-7 wt% are the Sealoflex materials used by Cass County. Asphalt mixes incorporating ground rubber crumb at 10-14% polymer plus rubber called Flexochape are produced by BAS Recycling in California.

GENERAL DATA ON MIXING RUBBER IN ASPHALT

The full potential of rubber in asphalt cannot be realized unless adequate mixing under good quality control is performed [16]. Both viscosity (60°C) and ductility at low temperature (4°C) are markedly improved when blending is done at higher temperatures. The usual procedure involves adding the rubber to molten asphalt at normal mixing temperature or higher, depending on the type. Since the asphalt by itself can be emulsified and cationic or anionic asphalt emulsions produced, for some purposes a cold mixing technique is applied in which the rubber latex would simply mix with the emulsified asphalt. For example, the latex is added at 130 to 150°C so that the aqueous portion of the latex suspension rapidly flashes off and the rubber particles are dispersed through the asphalt. Higher temperatures (155 to 180°C) are, however, used for mixing tire powders and asphalt. By the end of one hour reaction time, the Brookfield viscosity of the rubber modified asphalt should reach a plateau and remain constant during subsequent mixing and storage with little or no change in viscosity. If the blend cannot be used in the desired application within 2-4 hours, the shelf life may be extended several days by lowering the temperature to 150-155°C. Agitation is necessary during this storage period to prevent the rubber from separating from the asphalt. This is a primary indication that this rubbery material is somewhat incompatible with the asphalt. If the viscosity drops during storage, either a catastrophic phase separation is occurring or the asphalt has begun to depolymerize due to overheating.

The mixing operation is the most critical step in the preparation of rubber-asphalt blends. The methods employed seem to influence both the end-product and benefits gained. The following variations to the usual high temperature mixing procedure have been commonly used (in the US) to incorporate rubber into asphalt cements.

a) Crumb rubber. Early attempts included the mixing of relatively large particles of crumb rubber (8-20 mesh) into the final product. These particles remain as discrete "chunks" of rubber swollen at the surface by the maltenes in the asphalt composition. Aromatic kerosines are added to increase the workability of the asphalt-rubber binder, but at least 20% and often as much as 40-60% more asphalt is required to produce acceptable mixes [17]. The higher cost of these mixes limits their applications to the control of reflective stress cracking.

b) A "dry process" has been evaluated for dispersing larger rubber particles (1/16 to 1/8 inch) directly in the aggregate before the asphalt binder is added. The rubber is added at loadings of 3 - 4% of the aggregate; a special aggregate gradation is required to eliminate possible crumb clumping and premature stripping. The process calls for 1.5-3% more liquid asphalt than conventional hot mix [18]. Sold under the tradename "PlusRide", the mixture has been demonstrated to reduce the harmful effects of road icing and reduce the stopping distance on ice-covered roads by 25%.

c) An aggregate coating technique involves the addition of a special reclaimed rubber product to the heated aggregate in the pug mill (hot paving material mixer) before mixing the asphalt. The heat activated rubber additive quickly becomes liquid, thus coating and encapsulating each aggregate particle in a rubberized sheath. The interstitial asphalt in the pavement contains a small proportion of rubber additive, since one prime purpose of the elastomer in this case is to provide better adhesion between asphalt binder and aggregate (stone) surface.

d) Powdered scrap tires produced by a wet grinding process (80-200 mesh) can be employed in a dry process where the fine rubber powder is mixed with the aggregate before the asphalt binder is added. The high surface area of the powder allows rapid equilibration with the asphalt and a stable asphalt cement is produced. This procedure appears to be the most promising technique for producing rubber asphalt blends, but facilities for grinding tires to fine particles are limited. Rouse Rubber Industries (Vicksburg, Mississippi) is the closest known company engaged in the manufacturing of finely ground rubber and reclaim from scrap tires and other rubber wastes.

BASIC PRINCIPLES OF VISCOELASTICITY

Extensive research has been done over the last decade in studying the rheology of asphalt and asphalt concrete [19]. The implementation of the performance-related specifications for asphalt cements [20] 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 [21-23]. Dynamic shear tests are advantageous because the data can be acquired within the linear range of the asphalt in a loading mode 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 [21].

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 [24]. The shear stress σ and the deformation (strain) γ are related via the shear modulus G as follows:

$$\sigma = G\,\gamma \qquad \text{(eq. 1)}$$

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:

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

where: $i^2 = -1$

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

$$\sigma(t) = \sigma_o \sin \omega t \qquad \text{(eq. 3)}$$

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

$$\gamma(t) = \gamma_o \sin \omega t \qquad \text{(eq. 4)}$$

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). 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

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

The stress vector can be similarly considered to be the sum of two components. One component, $\sigma' = \sigma_o \cos \delta$, is in phase with the deformation, the other component, on the other hand, $\sigma'' = \sigma_o \sin \delta$, 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

$$G' = \sigma' / \gamma_o = (\sigma_o / \gamma_o) \cos \delta = G^* \cos \delta \qquad \text{(eq. 6)}$$

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

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

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

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

and

$$\gamma^* = \gamma_o ei(\omega t - \delta) \qquad \text{(eq. 9)}$$

The complex modulus G* may be then expressed as shown in equation 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

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

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

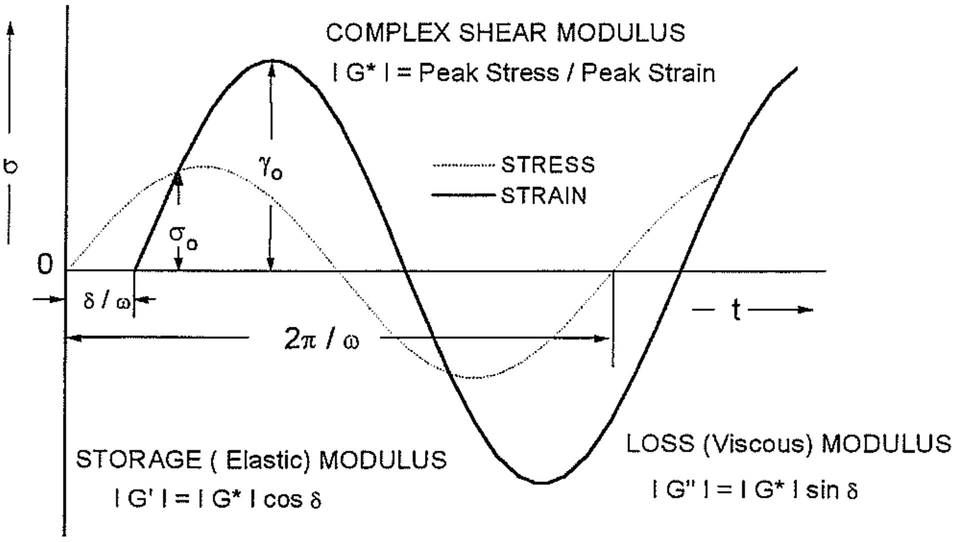

Figure 1. Schematic representation of the stress σ as a function of time t with dynamic (sinusoidal) loading (strain).

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:

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

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 2. 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:

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

and that

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

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 $|G^*|$, 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 $|G^*|$, 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 Tg 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.

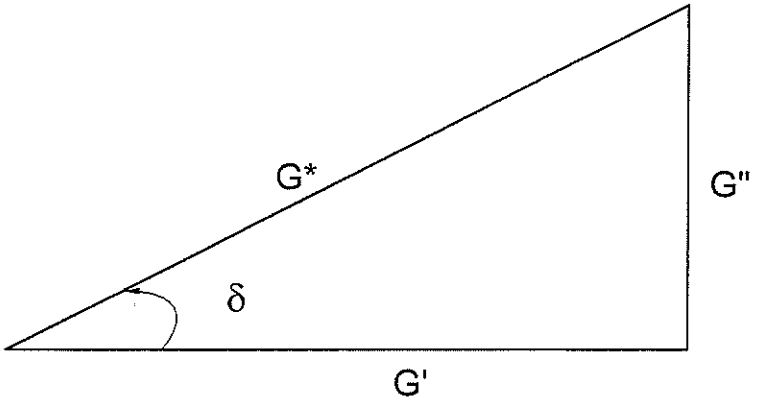

Figure 2. Relationships among dynamic moduli and the phase angle shown schematically through the trigonometry of a right triangle.

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) [25]:

$$\log(a_T)/(a_{Td}) = -C_1(T-Td)/(C_2+T-Td) \qquad \text{(eq. 15)}$$

where:

a_T/a_{Td} = the shift factor relative to the defining temperature, Td

C_1 & C_2 = empirically determined constants

T = the selected temperature, in °C or °K, and Td = the defining temperature, in °C or °K, which is a characteristic parameter for each asphalt cement; T_d is considered the threshold temperature to glassy state; 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 $C_2 = 56$ [25]. 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 [22]. 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 Tg causing an increase in G' modulus and a decrease in tanδ. 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 kinds of rheological master curves [19,21,22].

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 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. The complications associated with these measurements are discussed in a special section of this report.

OBJECTIVES AND SCOPE

1. To prepare a series of crumb and powdered rubber blends with Louisiana asphalts and assess the compatibility and stability of each blend.
2. To evaluate the potential for applying dynamic testing techniques to asphalt/rubber blends. The survey includes determination of rheological parameters, high temperature viscosity, and creep.
3. To subject the rubber asphalt blends to both TFOT and PAV aging to determine the hardening characteristics and compatibility of the blends during accelerated aging.

Blends of crumb vulcanized rubber with one AC5, seven AC10, one AC20, and ten AC30 asphalts using two differential mixing protocols were prepared. Corresponding blends of powdered rubber with one AC5, three AC10 and one AC20 asphalts were also prepared using the favored mixing protocol. Dynamic mechanical testing procedures were employed to characterize the rubber/asphalt blends. The tank asphalts and rubber/asphalt blends were subjected to aging by thin film oven testing followed by pressure aging and recharacterized using dynamic mechanical testing procedures.

METHODOLOGY

Asphalts. Tank asphalts provided by Louisiana refineries were used for the preparation of rubber/asphalt mixtures. Sample rubber blends were prepared using grades (number of sources) AC-5 (1), AC-10 (7), AC-20 (2) and AC-30 (10), and two different types of rubber particles. The distribution of components in selected samples was determined by solution NMR in perdeuterotetrachloroethane. A relaxation agent, $Cr(acac)_3$, 12 mg/ml, was added to the ^{13}C NMR samples [26]. Table 1 summarizes the observations on four samples of Louisiana asphalts; three different AC sources are represented in the samples. The relative crystallinity the asphalts as measured by DSC is also reported.

TABLE 1

NMR AND DSC CHARACTERIZATION OF ASPHALT COMPOSITIONS

Sample	Sunshine 5AC10	Southland 2AC10	Exxon 4AC10	Southland 20AC5
Arom H%	6.22	4.53	6.90	5.88
Arom C%	37.3	33.4	37.3	
Benzylic H%	14.89	5.62	14.89	12.30
Linear Aliph H%	78.89	89.85	81.73	81.82
Methyl/Aliphatic	21.22	30.08	20.95	26.14
ΔH_f, (J/g)	7.7	5.8	8.5	
% cryst.[a]	3.9	2.9	4.3	
Glass Transition Tg,(°C)	-12	-20	-3	

[a] Average entropy for 100% crystallinity = 200 J/g [27]

Polymeric Additives: Rubber from ground tires was used as received from the suppliers as crumbs (Baker Rubber Inc., Southbend, IN) or fine powder (Rouse Rubber Industries, Inc., Vicksburg, MS). The crumb rubber, CR, had a maximum particle size of 1.2 mm and contained residual polyester fiber particles; 25.7% of the particles did not pass a #20 mesh sieve (> 0.84mm) and 3.5% were retained on the #16 mesh (> 1.19 mm). The powder rubber, PR, was a fine 200 mesh (0.074 mm) ground rubber.

One of styrene(S)-butadiene(B) copolymers investigated as an additional asphalt additive was KRATON D1101(Shell), which is a linear SBS triblock copolymer of medium molecular weight containing 31% styrene. The block copolymer rubber was coded as BCR. It was mixed with asphalt cements with or without PR according to the protocol depicted in Figure 4. The devulcanized rubber asphalt mix (ECOFLEX, The Bitumar Group, Montreal, Canada) was a material completely soluble in aromatic hydrocarbons. No high molecular material could be isolated by precipitating fractionation using benzene as solvent and methanol as nonsolvent. The insoluble fraction in petroleum ether, i.e. the nonpolar components, amounted to 24.2%. It was mixed with PR and asphalt cements according to the protocol described for PR/AC blends.

A virgin styrene-butadiene copolymer, i.e., not vulcanized, was separated by precipitation with methanol as small crumbs (0.5 - 1 mm) from ULTRAPAVE SBR latex (Goodyear-Textile Rubber & Chemical Co.). The dried crumbs were then used in combination with CR to obtain blends according to the protocol described for CR/AC blending. The SBR containing blend was coded CoPolyR.

NOVOPHALT^R modified asphalt cement - a bi-phase binder system containing 4-6% polyolefin additives and paving grade asphalt cements - was our reference material, especially for isochronal representations and creep measurements. NOVOPHALT, introduced to this country in 1976, is used in place of conventional binders to improve the performance of asphalt concrete. Reducing of permanent deformation, particularly at elevated temperatures, the increase of the resistance to fatigue and the improving of the resilient modulus are the primary benefits of NOVOPHALT modified asphalt cements. The samples were coded Novophalt AC-10 or Novophalt AC-30, depending on the grade of the base asphalt used (Marathon AC-10 or AC-30).

Methods. The relative crystallinity of a given asphalt can be measured by DSC [28,29]. A Seiko DSC 220C calibrated for temperature and enthalpy with indium was employed to estimate the relative volume of the crystalline phase in each of the asphalt samples. The DSC was conducted on ≅ 10 mg samples sealed in an aluminum sample pan using an empty aluminum sample pan with cap as a reference. Initially each sample was cooled at 3°C/min to -45°C and then heated at 3°C/min. The heats of fusion (ΔH_f) observed are listed in Table 1. The percent crystallinity was estimated from this data by assuming that completely crystallized hydrocarbons in an asphalt matrix exhibit an average enthalpy of 200 J/g [27]. The glass transition temperatures, Tg, of the neat asphalts and of blends containing BCR, ECOFLEX, PR or CR were estimated by differential scanning calorimetry, DSC, using a SEIKO DSC 220 at a heating rate of 10°C/min. The glass transition was observed after the sample had been subjected to one heating/cooling cycle (RT→150°C→ -30°C).

A Brookfield viscometer (Spindle # 3) was used to evaluate the change in consistency of binders at high temperatures. Viscosity variations based upon both the amount of rubber added and the blending/storage times were measured. Bohlin CS and VOR rheometers and a Seiko DMS110 dynamic mechanical spectrometer were used to investigate the rheological behavior of neat, PMAC's and RAC's. Initial rheological measurements were made using a Bohlin CS rheometer and the measurements were made with a 4° cone and plate with a diameter of 20mm; the minimum gap was set at 0.15 mm. The Bohlin VOR measurements were made using 8 mm parallel plates at a gap of 2 mm. The SEIKO DMS employs a vertical parallel square plate system; the contact area of the plates was 100 mm^2 and a gap varying from 0.7 to 1.5 mm. A constant stress creep test was run at 35°C with the BOHLIN CS rheometer; the stress applied was 590 Pa. Creep recovery was measured after stressing the sample for 10, 100 and 1000 sec.

To generate a master representation of DMA data, multiple frequency determinations (Bohlin CS, f = 1,5,10,20,30; VOR; f = 1, 2, 5, 10, 20, 50 and 100 Hz) were used in the present study. The reference temperature was taken as T = 64 °C to comply with the performance graded asphalt binder specification [20] particularized for the hot climate typical of Louisiana. Using the WLF equation to estimate the shift factor, the best grouping of data was obtained when the values of C_1 and C_2 were 17 and 60, respectively.

Vulcanized Rubber/Asphalt Cement Blends. The rubber from ground tires was used as received from the suppliers as crumbs (Baker Rubber Inc., Southbend, IN) or fine powder (Rouse Rubber Industries, Inc., Vicksburg, MS). Blending was done with a high speed lab stirrer in aluminum containers normally used as soft drink cans. The cans were immersed in an oil bath maintained at T+5°C, where T is the mixing temperature. Particular blending protocols are depicted below. CR was added to AC at 220°C, the temperature was allowed to drop to T = 170°C and the blending was continued at this temperature for 40 min (Figure 3). PR was added to AC at T = 170°C and the blend was stirred for 20 min (Figure 4). The cooling to ambient temperature was not monitored. The cans were also used for the storage of blends.

Microscopic Observations. Asphalt samples were shaped as cylindrical rods ($l \approx 4$ cm, $\phi \approx 0.5$ cm) which were fractured after cooling to dry ice temperature (-78°C). The fractured surface was sampled out on a glass slide and examined immediately at room temperature by epifluorescing microscopy. This technique makes use of the fluorescing light (λ corresponding to green region) emitted by the sample upon illumination with light emitted by a mercury lamp (λ in the blue region).

Asphalt Aging. Representative asphalt and asphalt/rubber blend (both crumb rubber and powder rubber described above) specimens were selected for RTFO and PAV aging. RTFO bottles loaded with 35±0.5g material were subjected to aging in the oven at 163°C for 85 min under an air jet positioned to blow air (flow rate: 4,000 mL/min) into each sample bottle at its lowest travel position while being circulated in the carriage (rotation rate of the carriage: 15°/min). Pure asphalt samples were RTFO aged without any difficulties and were submitted to the next aging step in the PAV. Asphalt/rubber blends, containing especially crumb rubber, foamed excessively. Therefore, the RTFO test was discontinued and replaced with the thin film oven test (TFOT). New samples were prepared (50±0.5g material) which were aged in the TFOT oven at 163°C for 5 hr under a continuous air flow. A gross phase separation was noted in the case of certain asphalt/crumb rubber blends. All RTFO pure asphalt specimens and TFOT asphalt/rubber blend samples (50±0.5g each) were subjected to PAV aging at 100°C and 300 psi for 20 hr.

Bending Beam Rheometer Measurements The bending beam rheometer (Applied Test System, Butler, NC) was used to measure the low-temperature creep response of PAV aged tank asphalts and rubber/AC blends. 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 required calculations were performed by a software program supplied with the rheometer.

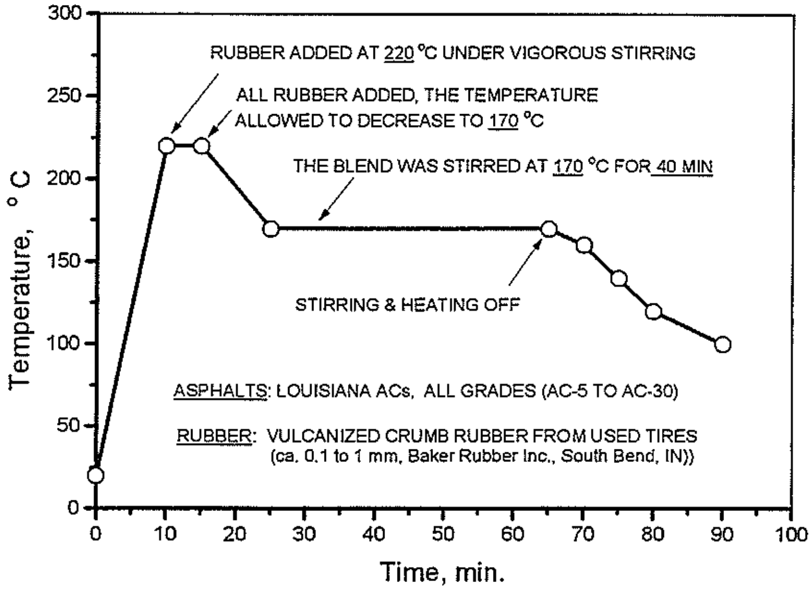

Figure 3. Protocol for blending asphalt cements with crumb rubber from used tires.

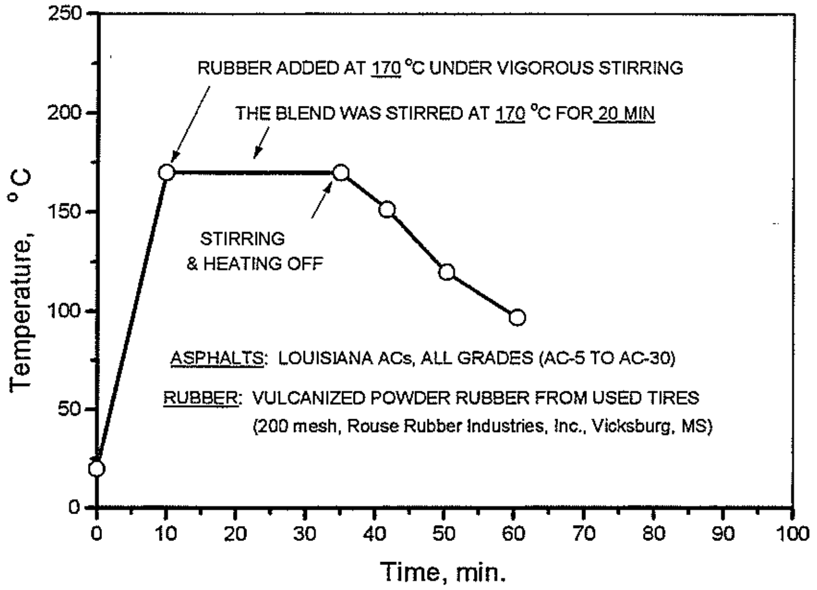

Figure 4. Protocol of blending asphalt cements with powder rubber from used tires.

RESULTS

CONSISTENCY OF RUBBER/ASPHALT CEMENT BLENDS

The polymeric additives usually have higher softening points than tank asphalt cements, thus, the consistency of the base asphalt at higher temperatures is increased. The increase of viscosity as a result of rubber addition depends significantly upon both the nature of the asphalt cement and the dimension of rubber particles. The viscosities of neat and polymer modified asphalt cements considered in the present investigation are listed in Tables 2 and 3.

A SHRP specification suggests that the viscosity of asphalt binders at 135°C should be less than 3 Pa·s in order to ensure pumpability at the hot mix asphalt plant. Higher viscosity blends may be employed if their workability and pumpability are demonstrated. AC-10 and AC-20 blends containing 15% crumb rubber could be produced within the 3 Pa·s specification. Powdered rubber enhanced the viscosity of the mixes more dramatically; values ranging between 4.01 and 6.76 Pa·s, which may not be acceptable, were recorded for higher rubber concentrations for AC10 blends, i.e., ≥15%. Therefore, the viscosities observed in blends containing 10% powdered rubber were compared with samples containing 15% crumb rubber in selected asphalts. Viscosities higher than 3.0 Pa·s were registered even at 170°C for 3AC30 at 15% CR and for 5AC10 blends with 20% PR.

The ratio of the asphalt/rubber blend viscosity to the tank asphalt viscosity was used to normalize the data in Figure 5. The variation in the viscosity ratio of AC-10 blends containing 15% tire rubber is quite extreme; increases relative to the corresponding tank asphalt viscosities ranged from 10 fold (for blends with PR) to 30 fold (for blends with CR). A similar variation was observed for PR/AC10 blends although of lower magnitude. Clearly, method specifications based upon asphalt grade and rubber content will not adequately predict the increased viscosity observed with asphalts from different sources. The specification should be expanded to include some measure of the chemical composition of both the rubber particles and the asphalt matrix.

TABLE 2

RHEOLOGICAL CHARACTERISTICS OF AC/POWDERED RUBBER BLENDS

Asphalt Source	SHRP Grade	Rubber, %	G*/sin δ, Pa⧗ @1 Hz & 64°C	Enhance Ratio	G" Pa @ 1Hz & 64°C	Ratio of G*20°C vs. G*64°C	Viscosity Pa's @ 135°C & 1 Hz
AC-5							
South. Lumb.	< 64	tank	396		393	166	0.08
20AC5			(776)				
"		2.5	838	2.12	838	144	0.45
"		5	2283	5.77	2166	103	0.70
"		10	4827	12.19	4289	49	1.02
"		17.5	9940	25.10	7712	36	5.0
"		20	11003	27.79	8821	32	6.76
AC-10							
South. Lumb.	64	tank	520		520	300	0.08
2AC10			(1535)				
"		5	2104	4.05	2036	103	0.18
"		10	5842	11.23	5184	63	0.89
Exxon	64	tank	898		909	383	0.10
4AC10			(2465)				
"		2.5	1165	1.3	1139	308	0.12
"		5	1279	1.42	1254	303	0.36
"		10	1701	1.89	1683	216	0.42
"		15	4343	4.84	4165	127	1.21
"		20	5462	6.08	5023	87	3.20
Sunshine Oil	<64	tank	592		568	492	0.21
5AC10			(845)				
'		2.5	1024	1.73	1024	256	
"		5	1310	2.21	1310	317	0.36
"		10	2080	3.51	2056	174	0.57
"		15	3811	6.44	3650	132	2.12
"		20	5397	9.12	5859	93	4.01
AC-20							
Star Enterpr.	64	tank	1145		1145		0.4
18AC20			(2400)				
"		2.5	2320	2.03	2315		0.86
"		5	3000	2.62	2932		1.01
"		7.5	3637	3.18	3513		
"		10	3819	3.34	3689		1.50

(⧗) Data in parentheses are extrapolated to 1.5 Hz

TABLE 3

RHEOLOGICAL CHARACTERISTICS OF AC/CRUMB RUBBER BLENDS

Asphalt Cement		G*/sinδ, Pa @ 64°C & 1.5 Hz	% CR	G*/sinδ, Pa @ 64°C &1.0 Hz	G*/sinδ, Pa @ 88°C &1.0 Hz	G* (20) / G*(64)	Viscosity @ 135°C &1.0 Hz, Pa.s
AC 5							
Southland Lumb.	20AC5	776	15	14,235		30	2.3
AC10							
Southland Sund.	10AC10	1470	15	13,221	1,580		2.0
Lion Oil Co.	16AC10	1683	15	6,622	532		1.5
Calumet.	21AC10	1376	15	6,830	711		1.9
Southland Lumb.	2AC10	1535	15	23,318	3,134	30	2.6
Exxon	4AC10	2465	15	9,964	1,086	69	1.8
Sunshine Oil	5AC10	845	15	5,692	643		2.0
Sunshine Oil	5AC10	845	17.5	14,714	2,210		2.5
Sunshine Oil	5AC10	845	20	20,766	3,464	36	6.8
Ergon	9AC10	812	15	11,814	1,260		1.9
AC20							
Star Enterpr.	18AC20	2400	15	13,320	1,139		3.0
AC30							
Southland Oil	11AC30	5320	15	1,2361	1,036		2.3
Southland Sund.	12AC30	88920	15	24,278	3,382		4.9
Sunshine Oil	14AC30	42101	15	18,835	2,691		3.1
Lion Oil Co.	15AC30	3740	15	13,786	2,691		2.6
Calumet	17AC30	4270	15	15,146	1,196		2.9
Marathon	1AC30	3900	15	20,195	1,341		3.0
Southland Lumb.	3AC30	3940	15	21,616	5,133		7.5
Coastal Mobile	6AC30	3495	15	18,722	1,916		4.5
Exxon	7AC30	4260	15	21,145	4,031		5.4
Ergon	8AC30	3077	15	13,935	1,266		2.6

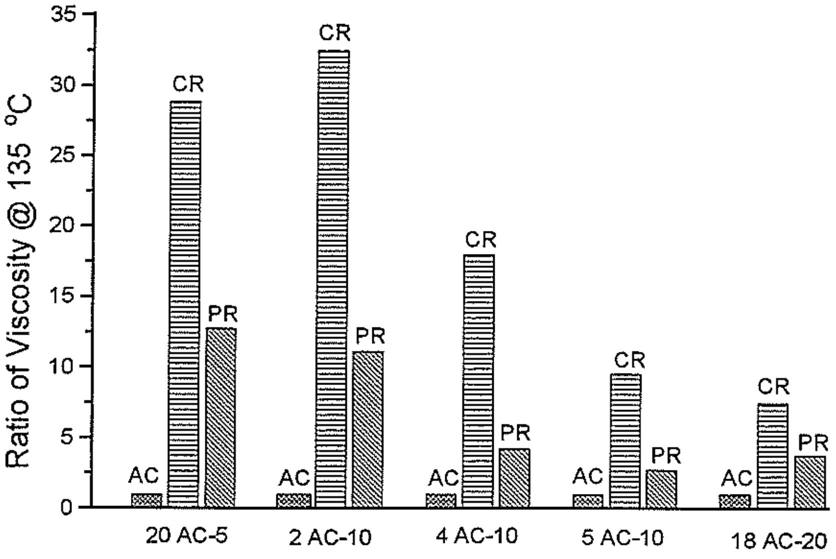

Figure 5. Viscosity variations produced by adding constant rubber content(15%) to different asphalts

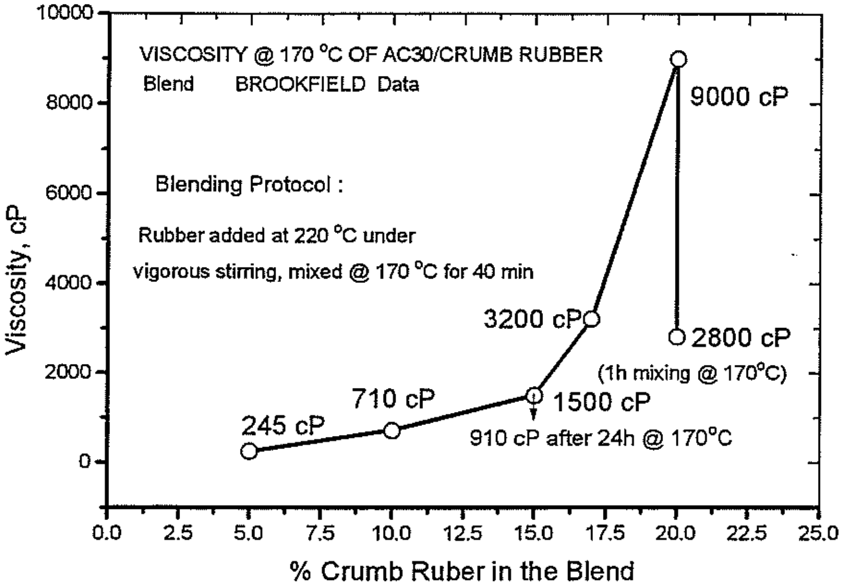

Figure 6. The effect of crumb rubber loading on high temperature viscosity of AC/CR blends.

Attempts to load high concentrations of rubber create unstable blends. The increase in viscosity produced by adding crumb rubber to an AC-30 asphalt is shown in Figure 6. At 15% CR the mixture is not stable; the initial viscosity of 1500 cP obtained after stirring at 170°C for one hour drops to 900 cP when the blend is held at 170°C for 24 hours. A more precipitous drop indicative of phase separation occurs when a 20% blend is stirred for 1 hour. The problems with blend stability noted in these experiments are indicative of the poor compatibility of simple asphalt rubber blends. It is our understanding now that the compatibility of vulcanized rubber with asphalt cements depends primarily on 1) the weight ratio of rubber to aspalt cement (i. e., the rubber concentration), 2) the nature and the grade of the AC used (i. e., its source and composition), and 3) the dimension of rubber particles (i. e., the smaller the particles, the larger the specific surface area and the higher the ability of rubber to absorb the light AC components). This compatibility problem will become more apparent in the discussion of the PAV aged samples.

Limitations of the Rheometers The dimensions of rubber particles significantly affect the rheology of the rubberized asphalts as indicated by variation in the phase angle, δ, with increasing temperature. The sin δ isochronal curves of both neat asphalt and powdered rubber asphalt cements (PRAC) approach one asymptotically as the materials begin to flow (Figure 7). The average dimension of the powdered rubber particles is 0.074 mm and satisfactory measurements could be obtained with a gap of 1.0 mm suggesting that if the particle size is less than 10% of the gap width the rheology of the blend can be determined. As a matter of fact, similar data have been obtained for PRAC samples with gaps of 0.4 mm ((ϕ =25 mm, cone and plate), 1 mm (ϕ =25 mm, parallel plates), and 2 mm (ϕ =8 mm, parallel plates), i.e., $G^*_{0.4mm} \cong G^*_{1mm} \cong G^*_{2mm}$ for the whole range of temperatures used (10-90°C). However, this is not the case for crumb rubber asphalt cements (CRAC) where $G^*/\sin\delta < G''$, i.e. $\sin\delta \neq 1$. In addition, the trend of sin δ at high temperatures is <0.9 indicating that the flow is far from Newtonian. This is due to limitations in the measuring technique since the rubber particles are somewhat large relative to the gap between the rheometer plates. In the cone and plate rheometer the maximum gap was only 0.4 mm; many rubber particles were twice this diameter. The parallel plate configuration with a gap of 2 mm should be less sensitive to interference from insoluble particles, but at high temperatures (> 60°C) the asphalt matrix begins to flow and the particles become the dominant contact with the rheometer plates. Thus, the elastic nature of the rubber particles is measured rather than the rheology of the matrix. These results indicate that the parallel plate configuration is not suitable for measuring asphalts modified with crumb rubber; a cup and disc configuration that would contain the asphalt matrix at higher temperatures is required. Thus, data obtained from PRAC's can be reasonably compared with other polymer modified asphalt cements, PMAC, but similar comparisons with CRAC's are not possible.

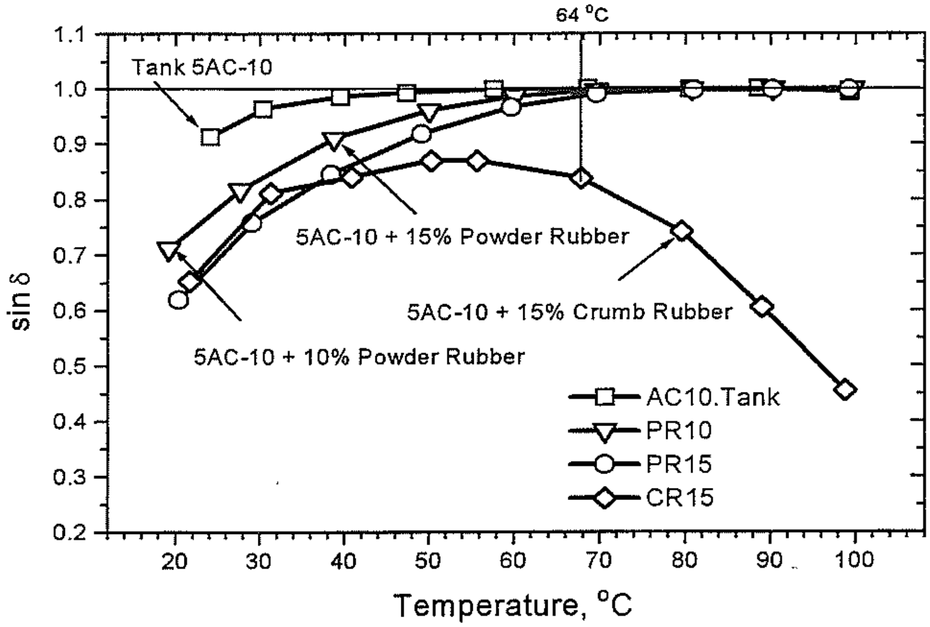

Figure 7. Plot of sin δ isochronal versus temperature for representative asphalt, powder rubber and crumb rubber asphalt blends.

There were some doubts regarding the accuracy of the temperature indicated by the thermocouple of the Bohlin VOR instrument. For example, the modulus values measured for the same AC30 material with the VOR instrument were much higher than that determined with the Bohlin CS rheometer. A second thermocouple (reading with a precision of 0.1°C, as required by the AASHTO standard) was inserted into the asphalt (or asphalt/rubber mixture) layer between the 8 mm parallel plates and both the values indicated by the instrument thermocouple and the additional thermocouple were recorded in an increasing temperature program. The results for tank asphalt is shown in Figure 8. The linear correlation is expressed as:

$$T_{corr} = A\,T_{obs} + B \qquad \text{(eq 16)}$$

where T is temperature in °C, A = 0.926 and 0.934 and B = 1.85 and 0.857 for tank and asphalt rubber blends, respectively. The corrected temperature values were then used for determination of all rheological characteristics of all types of binders.

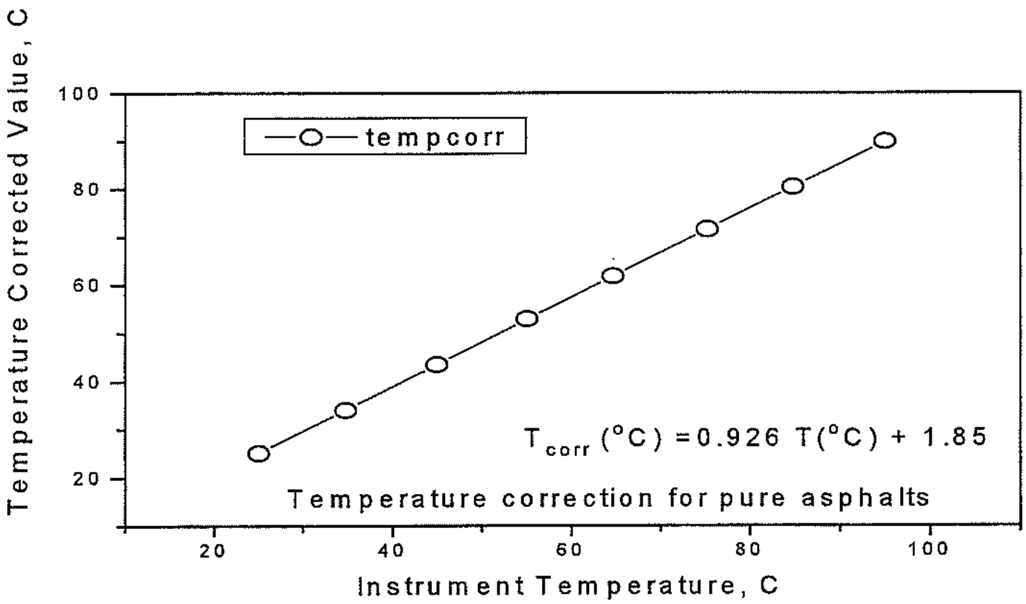

Figure 8. Temperature calibration curve for tank asphalt samples measured in Bohlin VOR machine.

RHEOLOGICAL EVALUATION OF RUBBER/ASPHALT BLENDS

According to the SHRP specifications, the contribution of the asphalt binder to fatigue cracking is optimized by specifying a maximum value for the stiffness parameter $G^*\sin\delta$ at the average pavement design temperature [20, 31]. However, since by definition $\sin\delta = G''/G^*$, it follows that $G^*\sin\delta = G''$; thus the loss modulus is indicative of this pavement distress. The basis for this relationship is the correlation of the dissipated energy with fatigue resistance, which has been shown to hold for over 100 different binder systems including PMAC's [30]. The dissipated energy, W_{dis} is defined as

$$W_{dis} = \pi \cdot \varepsilon^{2} \cdot E \cdot \sin\delta \qquad \text{(eq 17)}$$

For a strain controlled pavement, (ε = constant, $\sigma = \varepsilon^{\circ}E$, G = constant E), we find that W_{dis} is directly proportional to the loss modulus, G" or G'sinδ:

$$W_{dis} = \text{const.} \cdot \varepsilon^{2} \cdot E \cdot \sin\delta = \text{const. } G'' \qquad \text{(eq 18)}$$

Since the loss modulus is a measure of the viscous flow within a viscoelastic fluid, this parameter relates also to permanent deformation at high temperatures. King et al. [23] demonstrated that *G"* does indeed correlate quite well with results from the rutting simulator. Below certain values at the test temperature, there was an approximately linear relationship of rut depth to log(G").

The contribution of the asphalt binder to permanent deformation of asphalt mixes is considered in terms of the minimum value for the stiffness parameter, G*/sinδ, at a maximum pavement design temperature (i. e., 1000 Pa @ 10 rad/s). This parameter correlates to that portion of the accumulated, non-recoverable deformation occurring in a pavement that is attributable to the asphalt binder. The higher the value, the less deformable is the pavement and the greater the rutting resistance. In fact, the inverse of the loss compliance, 1/J" at 10 rad/s was the specification criterion for rutting resistance. Rather than introduce an additional term in the specification, the term G*/sinδ was used; G*/sinδ is numerically equivalent to 1/J" [31].

Effect of Asphalt Composition on Blend Properties. An inspection of Tables 2 and 3 shows that indeed there is no direct correlation between the AC grade and the SHRP stiffness parameter observed with rubber modified asphalt cements, RAC. Asphalts obtained for AC-5 mixes were particularly sensitive to the rubber content as indicated by the relative increase in stiffness, G*/sinδ(blend)/ G*/sinδ(tank) plotted in Figure 9. For example, addition of a small amount of rubber (2.5%) upgraded the asphalt cement as much as two grades in the AC5/PR series. In fact, modified asphalts from this source, using either 20AC5or 2AC10 blends, exhibited higher values for the G*/sinδ parameter than similar AC10 based blends derived from other sources. The effect is quite pronounced in samples modified with powdered rubber where the surface area is much higher than that of crumb rubber. Clearly, the chemical structure of the asphalt cements, in particular the propensity to penetrate and swell the rubber particles, must be taken into consideration if the properties of asphalt-rubber mixes are to be predicted. This observation is consistent with the observations on the effects of asphalt composition on blends of poly(styrene-*co*-butadiene) latexes with asphalts extended with aromatic oils; more extensive swelling was observed in asphalts with high aliphatic contents. [32]

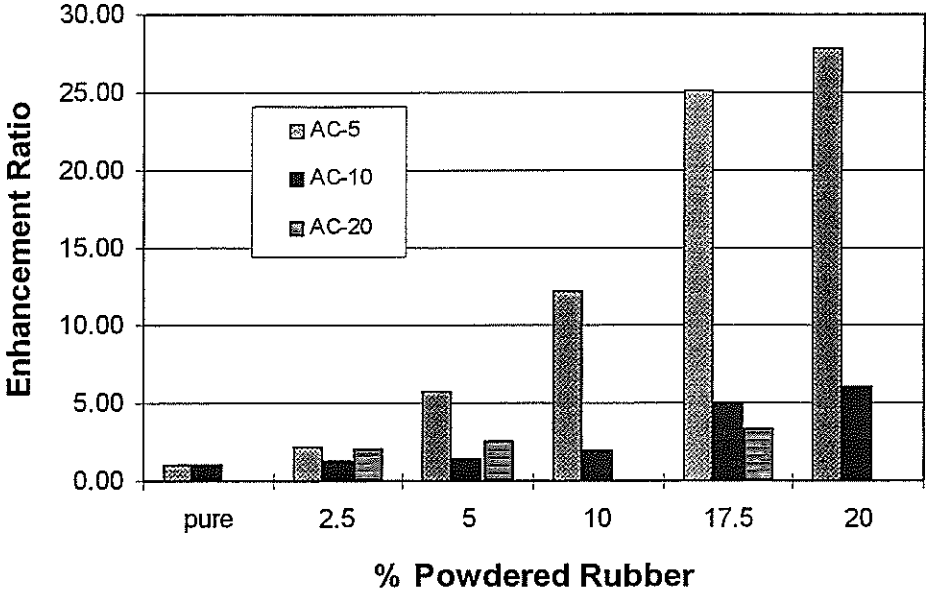

Figure 9. Relative enhancement of G*/sin δ compared to base asphalt G*/sin δ for asphalt/ powdered rubber blends.

In SHRP specifications, the contribution of the asphalt binder to permanent deformation of asphalt mixes is considered in terms of a minimum value for the stiffness parameter, *G*/sinδ*, (i. e., 1000 Pa @ 10 rad/s) at a maximum pavement design temperature. This parameter correlates to that portion of the accumulated, non-recoverable deformation occurring in a pavement that is attributable to the asphalt binder. The higher the value, the less deformable is the pavement. Isochronal plots of G*/sin δ reveal distinct differences in the contribution of the additives to the mix stiffness. In Figure 10, it is clear that the base asphalt would qualify for a maximum use temperature of 58°C; addition of at least 10% PR or CR raises the qualification to > 64

°C. Using tire powder or crumb rubber at 10 wt% enhances the high temperature properties without changing the low temperature properties extensively, i.e. the temperature susceptibility of the mixes are lowered.

The values of the stiffness parameter, G*/sinδ, (read at 64°C from isochronal plots at 1Hz of G*/sinδ versus temperature) are listed in Tables 2 and 3 for neat asphalt cements and mixtures prepared from the respective AC and powdered or crumb rubbers. First, it is important to note from Table 2 that all neat asphalt cements and most of AC/PR blends exhibit Newtonian behavior at 64°C, i.e. the storage modulus vanishes since at sin δ≅1, G*/sinδ ≅ G". In contrast, G*/sinδ does not correspond with G" for the measurements made on crumb rubber modified samples (Table 3).

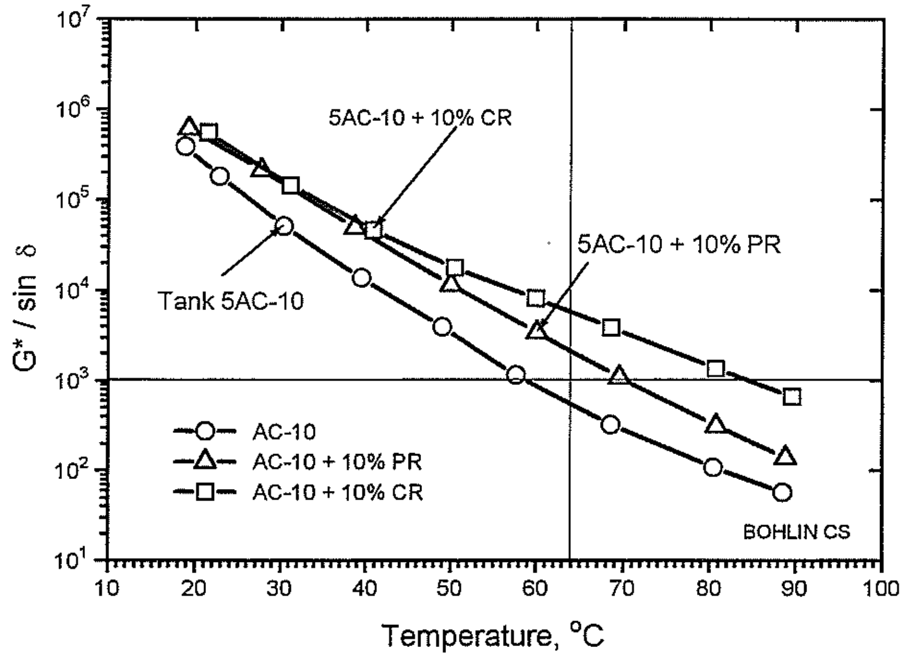

Figure 10. Isochronal plots of G*/sin δ for neat and rubber modified paving grade 5AC10 binders.

An estimate of the temperature susceptibility can be obtained from a ratio of the value of one of the moduli determined at low temperature vs. one measured at a much higher temperature [33]. We have elected to report the characteristic ratio of the complex moduli, G*20°C/G*64°C as this indicator. Not surprisingly, changes in the temperature susceptibility relative to neat asphalt reflects the additive compatibility as well. The change in the characteristic ratio, G*(20°C)/G*(64°C), is quite revealing; the mixes containing powdered or crumb rubber reduce the ratio by approximately 25% comparable to the neat asphalt.

As one might expect, vulcanized rubber can also improve elasticity (increase the storage modulus) of the asphalt binder and strengthen the asphalt - aggregate bond at high temperatures. Addition of 5% rubber is sufficient to produce markedly enhanced properties without raising the high temperature viscosity excessively. Depending upon the source of the asphalt, addition of 15-20% rubber can produce very stiff mixes. Since a swelling reaction takes place when the asphalt cements are mixed with vulcanized rubber, the degree of the interaction - and therefore the storage modulus of the blend - is mainly dependent upon the chemical composition of the AC and less on its grade. The properties of the single AC-5 asphalt evaluated were extremely dependent upon the rubber concentration. If this behavior is typical, the lower grade asphalts may be more effective in swelling the rubber particles and thus allowing the rubber to contribute more effectively to the properties of the blend. Further, since the rubber particles absorb the lighter fractions of the asphalt cement, this interaction could result in an increased binder viscosity and hence higher blend stiffness. Clearly, one cannot predict the elastic behavior of a rubberized asphalt based on the AC grade.

We selected four asphalts with different responses to rubber additives and evaluated them by ^{1}H NMR. The spectra could be divided into three regions, aromatic (6.5 - 8.5δ), polar (2.2 - 4.0δ) and aliphatic (0.5 -1.00δ); the relative areas indicative of the proton distribution among these regions are summarized in Table 1. Little correlation between the concentration of either aromatic or polar components with stiffness enhancement was observed. As expected, the total aliphatic proton composition appeared to be significant; compositions with higher aliphatic contents, i.e. the Southland mixes, exhibited the greater enhancements. A more comprehensive sampling will be required to confirm a correlation.

The impact of polymer additives on the shear loss modulus is illustrated by a master curve of G" vs frequency (Fig. 11). Since the properties of PMAC's are typically comparable with neat asphalts of higher grades than the asphalt used to prepare the mix, the shear loss modulus of an AC-30 asphalt is plotted together as a reference with that of the commercial Novophalt AC-10 blend. At low frequencies, corresponding to high temperatures, the higher viscosities of the PMAC's is apparent. The absolute values of *G"* of the PR modified AC-10 binder are comparable to that of the commercial blend (and of the CR/AC-10 blend at lower frequencies) and are superior to those of the higher viscosity grade AC-30 binder. At high frequencies (i. e., low temperatures), the properties of the CR/AC-10 blend fall below those exhibited by AC-30; it is expected that the field performances of mixes prepared with blended CR binders will be inferior to those based on PR/AC-10 mixtures. An AC-30 blend containing 17% CR, used on US#61 (Wakefield), had a high loss modulus even at 80°C, but at much lower temperatures, $T \leq 50°C$, the G" of the base asphalt (1AC-30) was higher (Figure 12). A similar trend has been registered for the variation with temperature of the SHRP stiffness parameter $G^*\sin\delta$ (which is the same with G") of an 5AC-10 blend containing a total of 17% rubber. Of these, 14% were CR and 3% were the random styrene-butadiene rubber CoPolyR (*vide infra*).

The variation of the shear loss modulus of asphalt rubber binders with the content of crumb rubber is shown in Figure 13. Note that the slope of the curve for the neat AC-10 and for the mixture containing 5% CR approaches 1 for a large domain of frequencies. This is the region of frequency (or temperature) where the flow properties of the binders exhibit Newtonian behavior, i. e. the fluid exhibits stress in proportion to the rate of the strain but not to the amount of strain. It is in this region that simple shear (cone and plate, sliding plate) and dynamic tests have been found to coincide [35]. Increasing the content of large rubber particles in the asphalt mixture produces both a deviation from Newtonian flow and an increase of the viscous component.

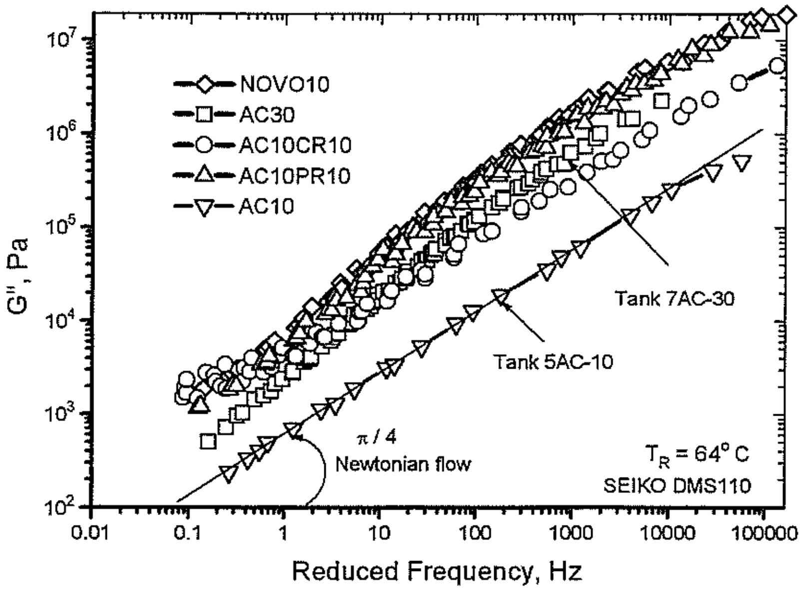

Figure 11. Plots of G" vs. reduced frequency for rubber modified paving grade 5AC10 binders. Reference materials: Novophalt AC-10 and 7AC30.

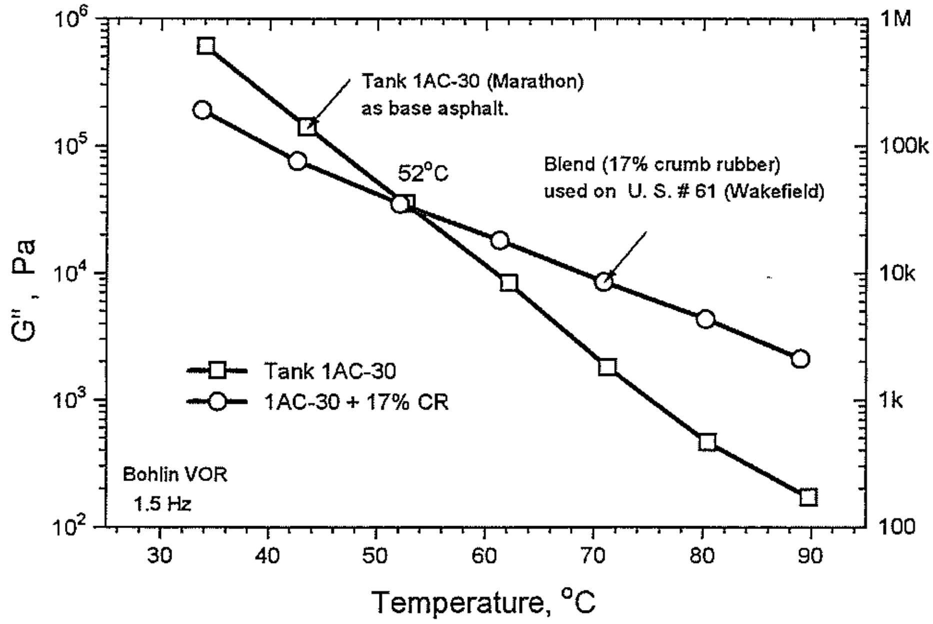

Figure 12. Comparative representation of loss modulus versus temperature for tank asphalt 1AC30 (Marathon) and the blend of 1AC30 with 17% CR used on US # 61 (Wakefield).

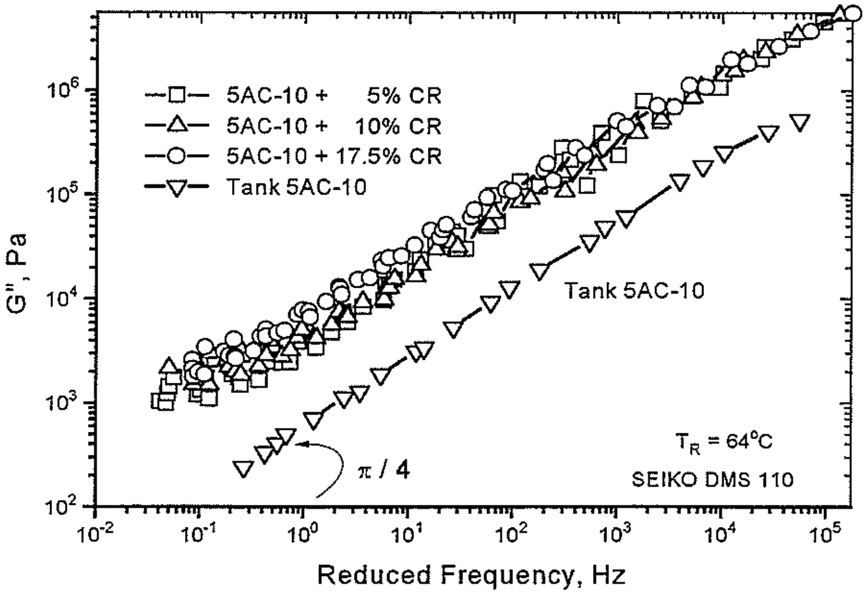

Figure 13. Plots of shear loss modulus, G", versus reduced frequency for 5AC10 tank and asphalt/rubber binders containing various amounts of crumb rubber.

Creep analysis. The constant stress creep/creep recovery tests (Figures 14-18) illustrate a much more pronounced difference between different polymer/AC blends than master or isochronal curves discussed above. The significant difference between the compliance of PRAC10 and CRAC10 mixtures might be an indication of their rutting resistance, i.e., the lower the 1/J value (Figure 14), which is directly proportional to the extent of deformation, the better the binder response to rutting. The Novophalt AC-30 material was completely resistant to creep under the conditions employed and thus would be expected to yield a cement with the maximum rutting resistance that can be imparted by the binder. The same conclusion can be drawn from the comparison of rigidity parameters listed in Tables 2 and 3. After long-term loading (1000 sec), none of the RAC's exhibited significant recovery, regardless of the asphalt grade (Figure 15). The asphalt matrix allowed some mode of slow stress relaxation that dominates over the expected stress recovery imparted by the presence of the more elastic fillers.

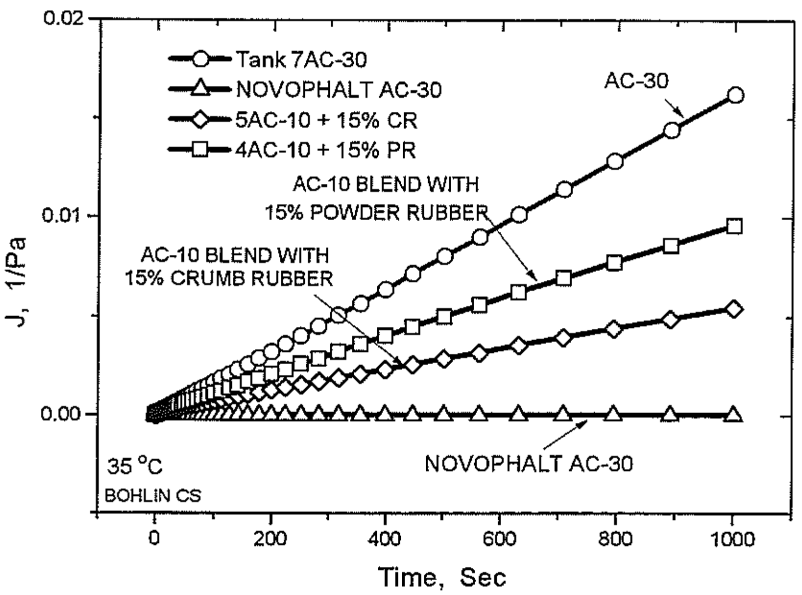

Figure 14. Constant stress creeping of AC-10 blends with 15% PR or 15% CR. Reference materials: 7AC30 and Novophalt AC-30.

Elastic creep recovery can be observed after short-term loading (10 sec) as illustrated in Figures 16. Since this recovery is primarily induced by the filler, one can observe distinct differences in the properties of the RAC's as the filler content is increased. Addition of 10% PR to and AC10 produced a blend with a creep recovery better than that of an AC30 from the same source. At first glance, the AC-10 blend containing 20% PR gave better results than the commercial PMAC Novophalt AC-10. However, for an accurate comparison, one has to consider the extent of deformation in each case for this particular loading time, as illustrated in Figure 17.

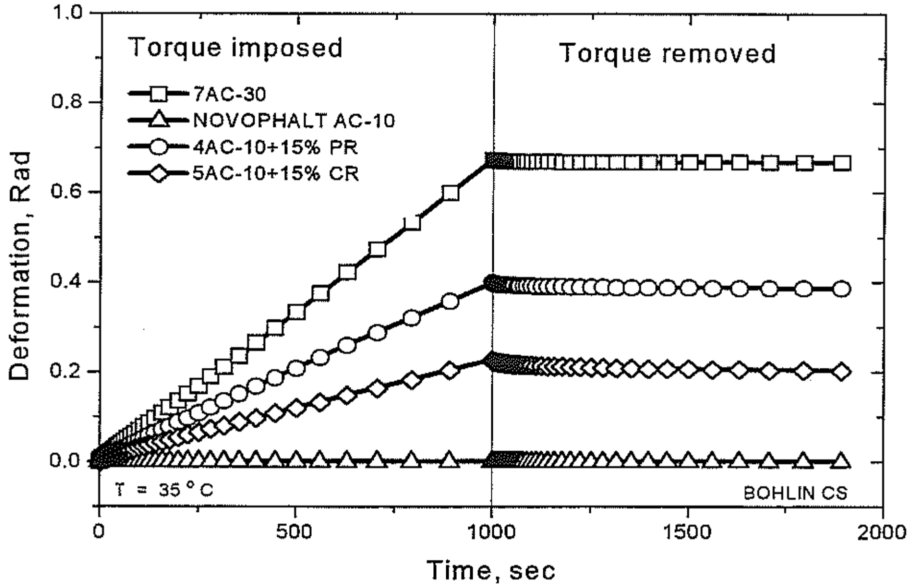

Figure 15. Constant stress creep/creep recovery curves at 35°C of AC-10 blends with 15% PR or 15% CR. Reference materials: 7AC30 and Novophalt AC-30.

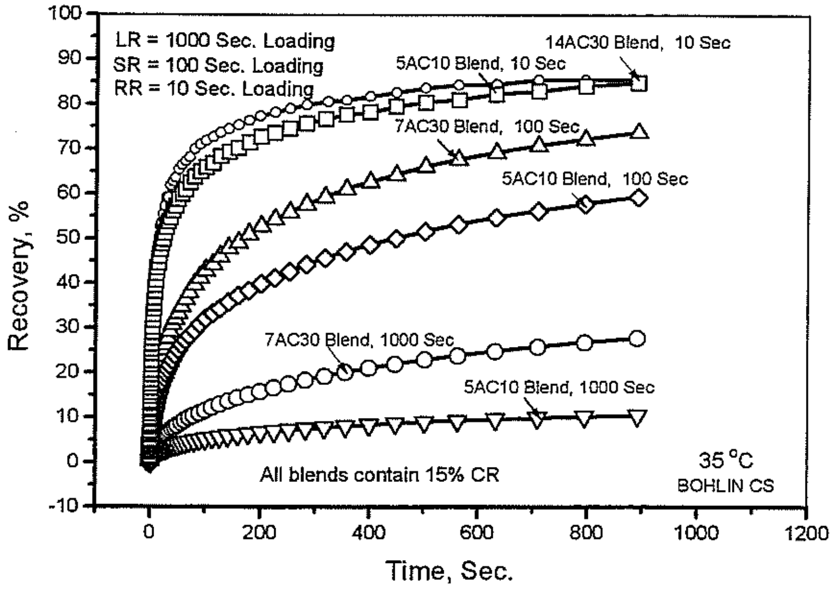

Figure 16. Extent of % recovery of 5AC10 and 7AC30 blends containing 15% CR after different loading times: 10 sec., rapid recovery (RR); 100 sec., slow recovery (SR); and 1000 sec., low recovery (LR).

The stress relaxation process is rather slow; creep recovery after medium term loading (100 sec, Fig. 18) is almost comparable to that observed after 10 sec loading considering that the sample deformation is greater. As expected, the reference AC-30 asphalt exhibited higher creep recovery than the AC-10 asphalt used for blending. Crumb rubber mixtures always displayed higher compliance and creep recovery than the corresponding mixtures with finely divided PR particles, regardless of the rubber content or the loading time. (Compare data from Figures 15-17 for 15% CR or PR content.)

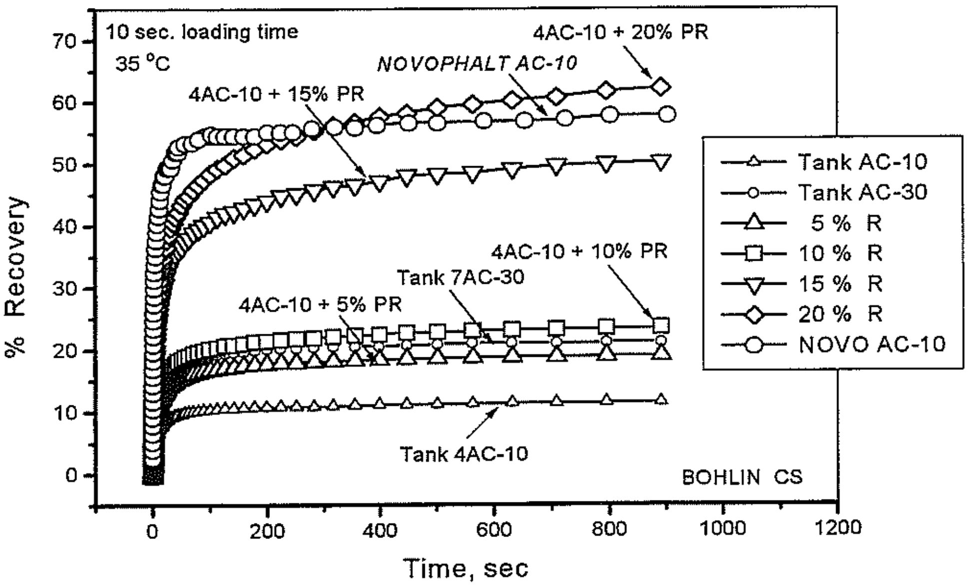

Figure 17. Creep recovery after 10 sec loading of PRAC10 blends. Reference binders: Novophalt AC-10, 4AC10 and 7AC30.

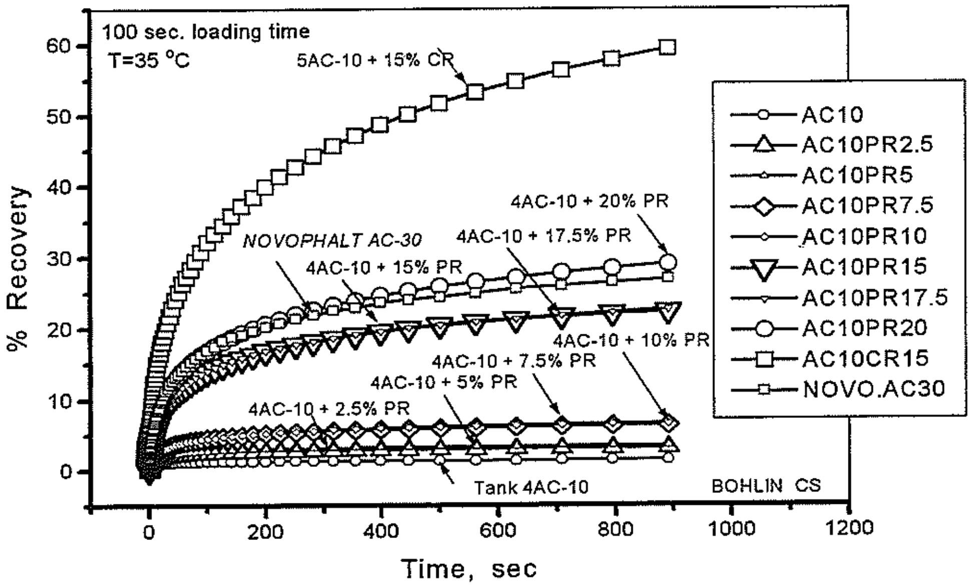

Figure 18. Creep recovery after 100 sec loading of RAC-10 blends. Reference binders: Novophalt AC-30 and Tank 4AC10.

Effect of Added Copolymers on Blends

Blends containing 2% SBS block copolymer (BCR) in addition to a 13% load of PR were prepared using either an AC-10 or an AC-30 base asphalt. The effect of BCR in AC-10 blends was beneficial especially at lower temperatures. Higher G"s, up to one or two orders of magnitude, were registered if compared to a blend containing 15% PR or to the base AC-10, respectively (Figure 19).

The blend containing 2% BCR and 13% PR, made with 14AC-30, exhibited a lower G" modulus than a 14AC30 blend containing only 7.5% PR, for the entire freqency (or temperature) sweep. However, the G" of the BCR containing blend was superior to that of the base asphalt with almost one order of magnitude, particularly at higher temperatures (or lower frequencies, see Figure 20).

The ECOFLEX binder was also blended with AC-10 and AC-30 grade asphalts. The AC-10 blend contained the same amount of ECOFLEX as the amount of base asphalt cement used (5AC10). The commercial ECOFLEX alone has G*/sinδ > 1kPa @ 70°C. Adding 10% PR or 15 % PR to an 1:1 ECOFLEX/AC-10 mixture almost doubled the value of SHRP stiffness parameter, G*/sinδ, at the same temperature, but this parameter was slightly inferior to a similar blend containing only AC-10 and 10% PR (Figure 21).

The same trend was recorded for the loss modulus of AC-30 blends containing ECOFLEX and 7.5% PR (Figure 22). It appears that the ECOFLEX components inhibit good interaction of the powdered rubber with the compatible fractions from the base AC.

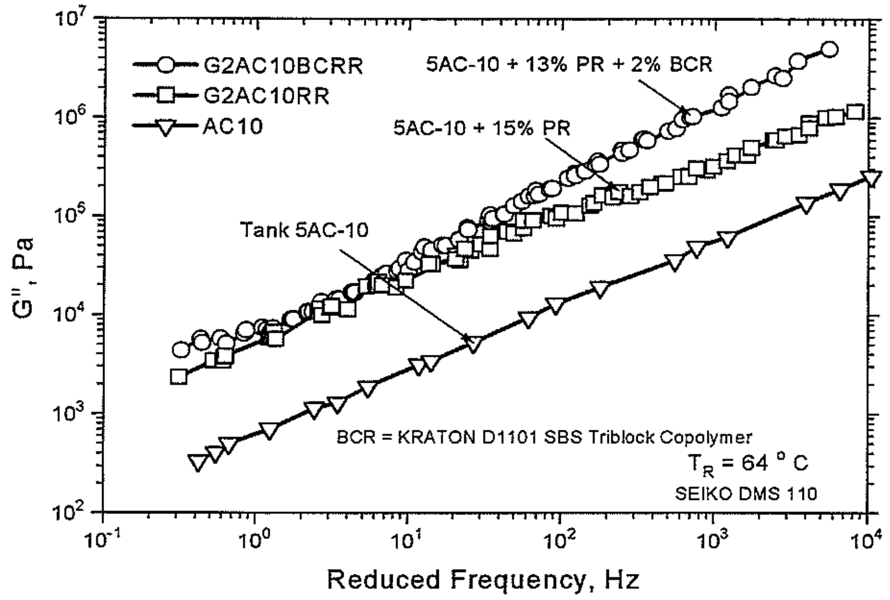

Figure 19. Comparative master plots of loss modulus vs. reduced frequency for 5AC10 blends with powder rubber and styrene-butadiene-styrene block copolymer.

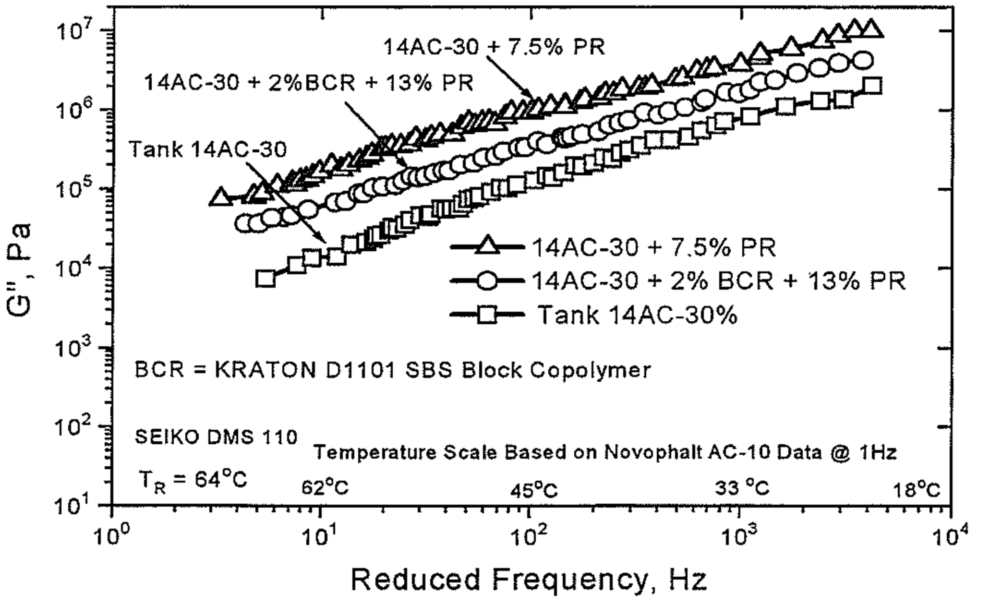

Figure 20. Comparative master plots of loss modulus versus reduced frequency for 14AC30 blends with powder rubber and KRATON D 1101 styrene-butadiene-styrene triblock copolymer.

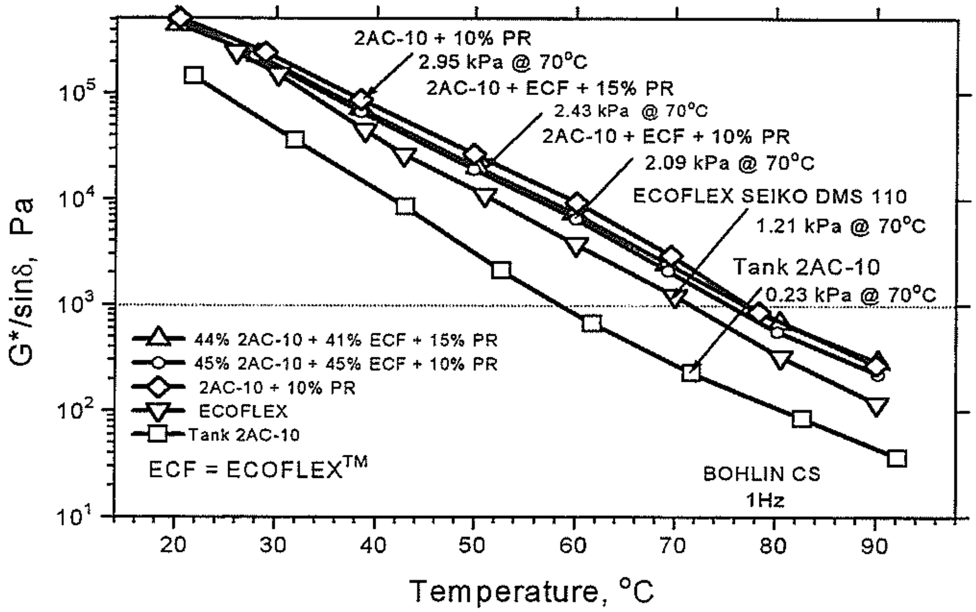

Figure 21. Comparative representation of G*/sinδ for blends of 2AC10 with ECOFLEX and powder rubber.

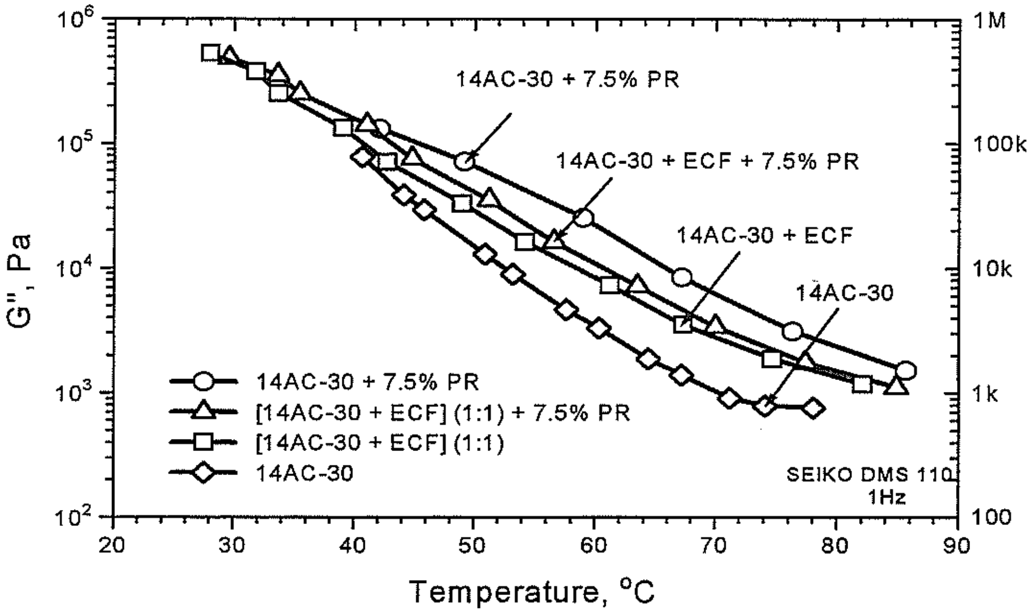

Figure 22. Comparative representation of loss modulus for blends of 14AC30 with ECOFLEX and powder rubber.

AGING OF ASPHALTS AND ASPHALT/RUBBER BLENDS

The SHRP specifications for binders comprise methods of testing in conditions that simulate critical stages during the binder's life. The three most critical stages are recognized as the following [34]: a. during transport, storage and handling, b. during mix production and construction, and c. after long periods in pavement. Tests performed on unaged asphalt binders represent the first stage. The second stage is simulated by aging the binder in a rolling thin film oven (RTFO), as detailed in AASHTO T-240 (ASTM 2827), or a thin film oven test (TFOT), ASTM D1754. These tests expose films of binder to heat and air and approximate the exposure of asphalt to these elements during plant mixing and handling. The third stage of binder aging is simulated by use of a pressure aging vessel (PAV). This test exposes binder samples to heat and air pressure in order to simulate, in a matter of hours, years of in-service aging pavement. Since binder samples aged in a PAV have already been aged in a RTFO, PAV residue represents binder exposed to all conditions to which binders are subjected during production and in-service time.

Because the RTFO and PAV protocols are considered aging techniques, no test results are required to be reported, with the exception of mass loss after RTFO aging (SHRP specifications allow no more than 1% mass loss for all binder grades). However, the SHRP specifications for the permanent deformation (rutting) and for the fatigue cracking of asphalt binders require determination of G* and its components for PAV aged materials (at a frequency of 10 rad/sec, which corresponds to 1.59 Hz). The rutting is related to the ratio $G^*/\sin\delta$, which must be at least 1.0 kPa for the original asphalt binder and 2.2 kPa after RTFO aging at the reference temperature. On the other hand, the product $G^*\sin\delta$ (or G") is used in the SHRP asphalt specifications to help estimate fatigue in asphalt pavements. The ability to dissipate or relax stress is a desirable binder trait in resisting fatigue cracking. Since it is anticipated that PAV aging will induce extensive hardening of the mixes, a maximum limit of 5,000,000 Pa (5,000 kPa) is listed in the SHRP specifications for $G^*\sin\delta$ at a low temperatures. Preliminary low temperature data using a bending beam rheometer confirmed that the rubber/asphalt blends met performance criteria at -12°C (Table 8), however, the instrument was not available during most of the period when this research was conducted. Therefore, the properties of the aged samples were evaluated using the Bohlin VOR and an estimate of the impact of PAV aging on the asphalt/rubber mixes was obtained.

TABLE 4

RHEOLOGICAL CHARACTERISTICS OF UNAGED AND PAV AGED ASPHALT BINDERS: AC5-20 (SOUTHLAND LUMBERTON) BLENDS WITH CRUMB RUBBER (CR); DATA @ 64°C & 1.5 HZ.

ASPHALT BINDER	G*, Pa	G", Pa	G*/sinδ, Pa
20AC5	761	669	776
20AC5. PAV	18,876	16,356	20,215
20AC5.15%CR	19,215	15,552	23,797
20AC5.15%CR. PAV	49,947	32,694	74,309

Two extreme cases were encountered. The first example is illustrated by the data in Table 4, which shows the high sensitivity of 20AC5 to aging. PAV treatment of the tank asphalt increased G" almost 25 fold from an initial value of 669 Pa. The PAV treatment was equivalent to adding 15% crumb rubber to the mix. Subsequent aging of the asphalt/rubber mixture induced a further two fold increase in the loss modulus. The magnitude of the changes observed indicate that the mixture remained compatible during the treatment, but it would undergo extensive age hardening in the field.

The second extreme case, gross phase separation, was observed after thin film aging of the Southland Sunderville AC-10 blend. PAV treatment was not required to effect blend separation. The example is interesting because the data on initial blend indicated that extensive swelling of the rubber particles had occurred. Blending 15% crumb rubber in the asphalt raised the loss modulus by almost 30 fold. After PAV aging the observed G" was only 1/15th of the initial value and less than that of aged tank asphalt. The drastic reduction in the loss modulus must be attributed to separation of the rubber component from the asphalt matrix. The loss of properties becomes more apparent at lower temperatures as shown in Figure 23.

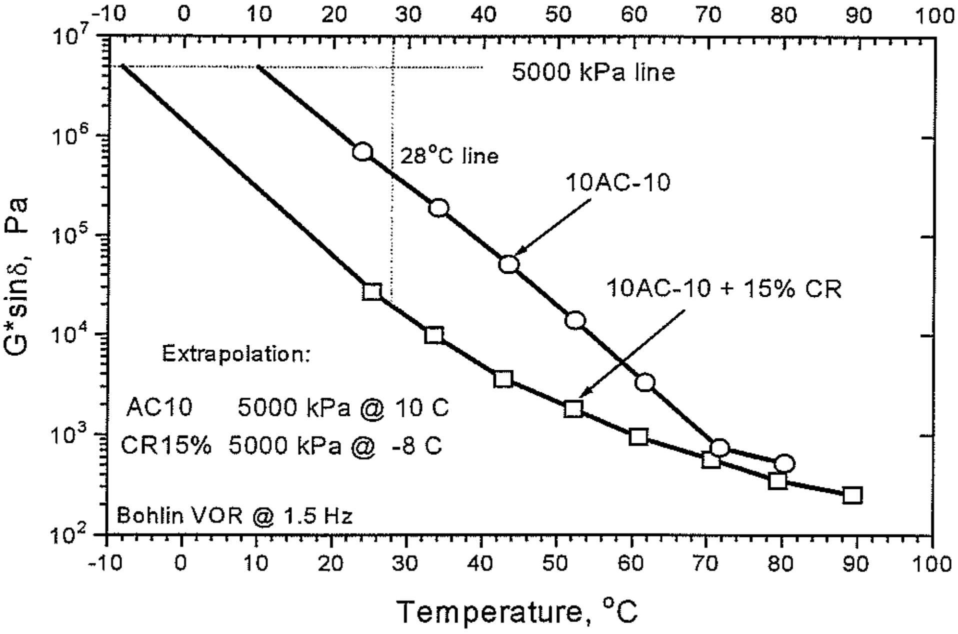

Figure 23. Comparison between Southland Sunderville 10 AC10 asphalt binder and a blend with 15% crumb rubber after PAV aging.

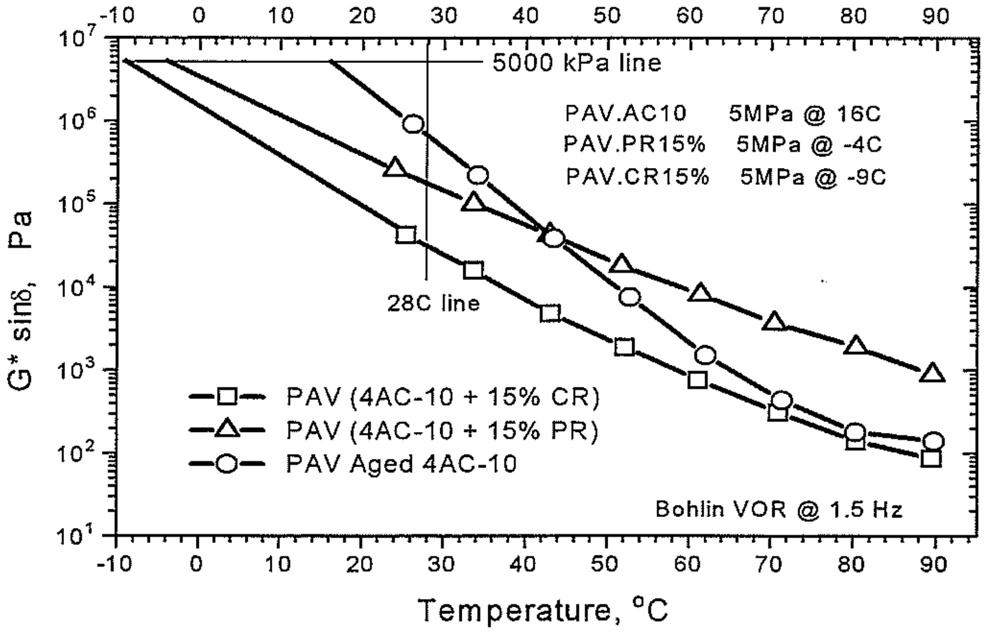

Figure 24. Comparison between Exxon 4AC10 asphalt binder and blends with 15% crumb rubber or 15% powder rubber after PAV aging.

TABLE 5

RHEOLOGICAL CHARACTERISTICS OF UNAGED AND PAV AGED AC10 GRADE ASPHALT BINDERS: 9 AC10 (ERGON), 10AC10 (SOUTHLAND SUNDERVILLE), AND 21AC10 (CALUMET) BLENDS WITH CRUMB RUBBER (CR); DATA @ 64°C & 1.5 HZ.

ASPHALT BINDER	G*, Pa	G", Pa	G*/sinδ, Pa
9AC10[a]	812	812	812
9AC10. PAV	726	675	784
9AC10.15%CR[a]	13,674	11,362	16,635
9AC10.15%CR. PAV	8,947	7,135	10,034
10AC10 [a]	1470	1470	1470
10AC10. PAV	2,540	2,340	2,787
10ac10.15%CR[a]	13,296	12,068	14,921
10AC10.15%CR. PAV[b]	1,088	804	1,471
21AC10	1376	1260	1439
21AC10. PAV	5,310	5,310	5,310
21AC10.15%CR[a]	8,004	6,801	9,899
21AC10.15%CR. PAV[b]	146	115	2137

a) Values extrapolated from 1Hz to 5Hz measurements (Bohlin CS instrument)

b) Gross phase separation observed during TFOT aging.

As Figure 24 illustrates, an analogous phase separation occurs upon PAV aging of crumb rubber blends prepared from Exxon AC10. The loss modulus is consistently less than that of the aged tank samples. Blends of crumb rubber prepared from Ergon and Calumet AC10's were also incompatible (Table 5). It appears that direct mixing of crumb rubber with Louisiana asphalts will not produce blends with long-term stability unless an additive that stabilizes the blend is found. Such an additive might be a random SBR, as illustrated in Figure 25. Replacing 3% of CR with a styrene-butadiene random copolymer (CoPolyR) in a blend containing 17% CR and 5AC10 as the base asphalt has a beneficial effect on the blend properties before and after PAV aging. The stiffness of the blend is higher than that of the base asphalt at T>50°C.

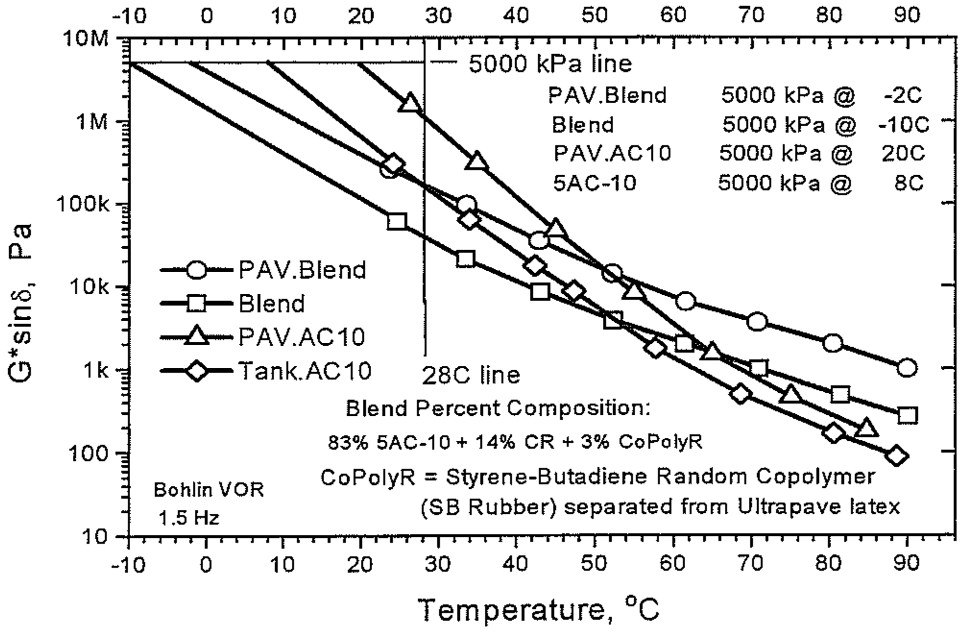

Figure 25. Comparative representation of G*sinδ for PAV aged blends of 5AC10 with CR and styrene-butadiene random copolymer (CoPolyR) separated from latex.

The stability of crumb rubber blends with higher grade asphalts was evaluated using a Sunshine AC30 binder. Addition of 15% crumb rubber raised the G" approximately 8 fold so the asphalt did swell the rubber particles. However, phase separation was noted after the TFOT aging and the G" of the PAV aged blend was less than that of PAV aged tank asphalt. The data from these experiments are summarized in Table 6.

TABLE 6

RHEOLOGICAL CHARACTERISTICS OF UNAGED AND PAV AGED ASPHALT BINDERS: AC30 (SUNSHINE OIL CO.) BLENDS WITH CRUMB RUBBER (CR). BOHLIN VOR INSTRUMENT. DATA @ 64°C & 1.5 HZ.

ASPHALT BINDER	G*, Pa	G", Pa	G*/sinδ, Pa
14AC30	1,738	1,738	1,738
14AC30. PAV	8,532	8,532	8,532
14AC30.15%CR[a)]	17,514	14,635	21,347
14AC30.15%CR. PAV[b)]	2,467	2,022	3,111

[a)] Values extrapolated from 1Hz to 5Hz measurements (Bohlin CS instrument)

[b)] Gross phase separation observed during TFOT aging.

In contrast, aged blends of asphalt and powdered rubber appeared to remain compatible. At high temperatures the loss modulus of the asphalt/PR blend remained higher than that of the aged tank sample (Figure 24). However, the powdered rubber was effective in reducing age hardening; at temperatures below 40°C, the loss modulus of the mixture was less than that of the tank asphalt. Extrapolation of the data to the temperature at which G*sinδ reaches 5,000 kPa illustrates this point. The intercept of the extrapolation is up to 25°C less than the corresponding intercept of the extrapolated aged asphalt data. Further, the apparent decrease in low temperature hardness was directly proportional to the rubber content. Partially compatible mixtures containing up to 20% PR were prepared (Figure 26). The data are somewhat scattered and the G" of the 15% PR sample was less than that of the original blend so partial phase separation occurred in this series (Table 7). However, if compatible asphalt/rubber blends can be prepared, the rubber additive will reduce the propensity for long-term low temperature cracking.

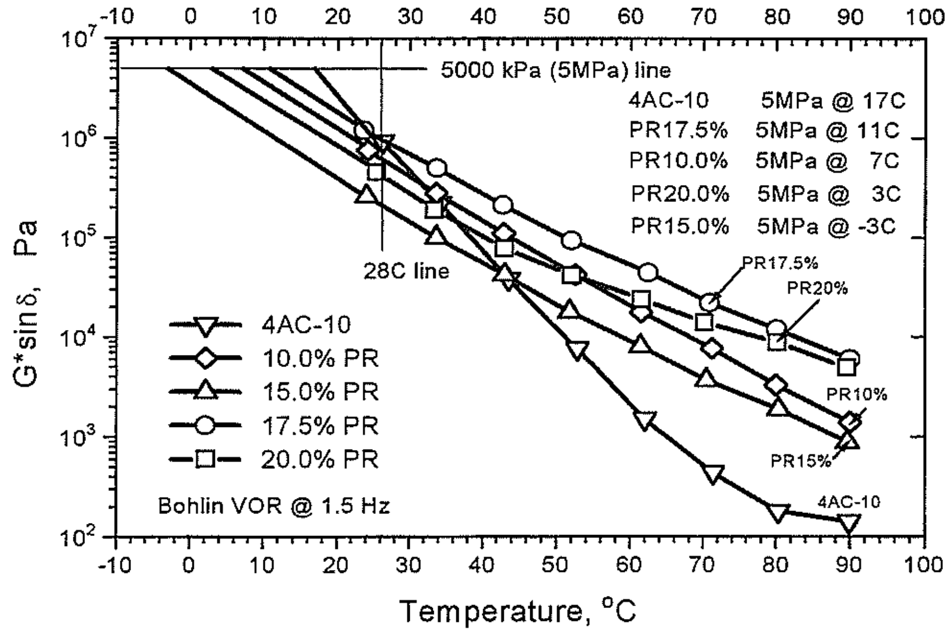

Figure 26. Comparison of stiffness of PAV aged Exxon 4AC10 asphalt binder and blends with 10, 15, 17.5, and 20% powder rubber.

Low Temperature Creep Response of Asphalt/Rubber Blends. According to SHRP recommendation, when BBR test data are used to verify the grade of an asphalt cement binder, the stiffness *S(t)* and the creep rate m = d log*S(t)* / d log*(t)* are reported at the specification temperature at 60 sec. If $S(t) \leq 300$ MPa, and $m \geq 0.30$, the sample meets the specified grade. If $S(t) \geq 300$ MPa and/or $m < 0.30$, the sample fails the specified grade. Since the minimum grade temperature for Louisiana asphalt binders is recommended as -10°C, the data were collected at the next lower SHRP grade temperature, -12°C. Representative results are presented in Table 8.

An inspection of Table 8 indicates that all blends met the *S(t)* and *m* criteria for the chosen temperature (-12°C). Rather large *m* values accompanied by low *S(t)*'s were recorded for some CRAC samples, suggesting that these blend might meet the criteria for much lower temperatures. However, the effect on the measurements of large rubber particles within the samples has not been resolved.

TABLE 7

RHEOLOGICAL CHARACTERISTICS OF UNAGED AND PAV AGED ASPHALT BINDERS: AC10-4 (EXXON) BLENDS WITH CRUMB RUBBER (CR) AND POWDER RUBBER (PR); DATA @ 64°C & 1.5 HZ.

ASPHALT BINDER	G*, Pa	G", Pa	G*/sinδ, Pa
4AC10[a)]	1470	1470	1470
4AC10. PAV	1,025	1,025	1,025
4AC10.15%CR	12,904	11,237	14,332
4AC10.15%CR. PAV[b)]	660	583	748
4AC10.10%.PR	2,047	2,040	2,060
4AC10.10%.PR. PAV	17,450	14,644	20,794
4AC10.15%.PR	8,758	8,688	8,826
4AC10.15%.PR. PAV	8,571	6,463	11,335
4AC10.17.5%.PR	7313	6,867	7,803
4AC10.17%.PR. PAV	55,222	38,403	73,901
4AC10.20%.PR	15,483	14,108	16,955
4AC10.20%.PR. PAV	30,183	20,855	43,556

a) Values extrapolated from 1Hz, 5Hz and 10Hz measurements (Bohlin CS instrument)

b) Gross phase separation observed during TFOT aging.

TABLE 8

LOW TEMPERATURE BBR CREEP DATA FOR AGED ASPHALT BLENDS WITH CRUMB RUBBER (CR) AND POWDER RUBBER (PR) (-12°C)

Asphalt Binder	Load P, g	Deformation δ, mm	Measured $S_{(60s)}$, MPa	Estimated $S_{(60s)}$, MPa	*m* value
4AC-10	100.2	1.475	101.78	101.72	0.3593
4AC10.15%PR	100.4	2.568	63.90	63.86	0.3220
4AC10.17%PR	100.9	2.708	60.90	6042	0.4938
4AC10.15%CR	100.3	1.812	90.47	89.40	0.4955
5AC10.10%PR	100.2	2.328	70.35	69.87	0.3986
5AC10.15%CR	100.3	1.179	139.05	130.17	0.6863
10AC10.15%CR	100.7	1.606	102.49	100.96	0.5648

CONCLUSIONS

The chemical composition of the asphalt is a very important parameter in determining the physical properties of RAC's. Asphalts with high aliphatic contents can induce excessive swelling of the rubber particles with a corresponding order of magnitude increase in the rheological properties.

Blends of vulcanized rubber particles can be analyzed using dynamic mechanical rheological techniques if the particle size is less than 1/10 of the gap between the plates of the rheometer. This was demonstrated by evaluation of powdered rubber blends. If the average particle size approaches the width of the gap, anomalous results may be obtained.

Addition of ground rubber particles to asphalt affects the performance related properties of the rubber-asphalt cement as follows:

1. The stiffness of the blend as reflected by $G^*/\sin\delta$ can be enhanced several fold depending upon the concentration of rubber added. This should improve the rutting resistance of the RAC's.
2. The increase in the loss modulus is parallel to the increase in stiffness. If the maximum value for G" is considered 3000 Pa @ 64°C for example, the concentration of rubber which may be added to a given asphalt is limited to approximately 10%.
3. The high temperature viscosity increases significantly when the rubber content exceeds 10%. The ability to prepare RAC's with 15% rubber that exhibit η @ 135°C less than 3.0 Pa·s depends upon the chemical composition of the asphalt and the rubber particle size.
4. Creep and creep recovery (resiliency) of RAC's are directly dependent upon the rubber content. These tests may be the most effective method for assessing the rubber/asphalt interactions.
5. PAV aging of asphalt/crumb rubber blends reveals that these blends will exhibit long term incompatibility. Asphalt/powdered rubber blends appear to be more compatible even after PAV aging and the low temperature properties of these blends suggest that the rubber imparts improved cracking resistance.

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