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TEXAS TRANSPORTATION INSTITUTE

Investigation of the Microstructural Mechanisms of Relaxation and Fracture Healing in Asphalt

Prepared for the Air Force Office
of Scientific Research

Annual Report
Grant No. AFOSR-89-0520
(2nd Year of a 3-Year Grant)

October 30, 1991

TEXAS TRANSPORTATION INSTITUTE
THE TEXAS A&M UNIVERSITY SYSTEM
COLLEGE STATION, TEXAS

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UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
N/A UNCLASSIFIED

1b. RESTRICTIVE MARKINGS
N/A

2a. SECURITY CLASSIFICATION AUTHORITY
N/A

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE
N/A

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release,
distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Texas A&M University
Texas Transportation Institute

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Texas A&M Research Foundation

6c. ADDRESS *(City, State and ZIP Code)*
Suite 508, TTI/CE Building
Texas A&M University
College Station, Texas 77843-3135

7b. ADDRESS *(City, State and ZIP Code)*
Texas A&M Research Foundation
P.O. Box 3578
College Station, Texas 77843

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
AFOSR

8b. OFFICE SYMBOL *(If applicable)*
NA

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR-89-0520

8c. ADDRESS *(City, State and ZIP Code)*
Bolling AFB
Washington, D.C. - 20332-6448

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
61102F	2302	DS	

11. TITLE *(Include Security Classification)*
Investigation of the Microstructural Mechanism of Relaxation and Fracture Healing in Asphalt Concrete.

12. PERSONAL AUTHOR(S)
Dallas N. Little, S. Prapnnachari and Allen Letton

13a. TYPE OF REPORT
Annual

13b. TIME COVERED
FROM 8-15-90 TO 9-15-91

14. DATE OF REPORT *(Yr., Mo., Day)*
10-30-91

15. PAGE COUNT
46

16. SUPPLEMENTARY NOTATION
This is the second year of a three year grant.

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Fracture healing, FTIR, asphalt, micromechanisms of fracture, asphalt modification, viscoelastic correspondence principle.

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Three research issues are addressed: (1) establishment of a mechanism of chemical healing of microcracks within the process zone preceding the macrocrack, (2) establishment of the mechanism or mechanisms of relaxation and creep in asphalt cements of various types and (3) establishment of a formal tie between permanent strain in asphalt concrete and cyclic loading and the creep compliance function.

A methodology has been developed by which to quantify the degree of fracture healing that occurs in asphalt concrete. The methodology has been verified by testing thirteen different asphalts with widely varying compositions and chemistries. This method of establishing the amount of fracture healing that occurs in asphalt concrete as the result of rest periods is being used to establish the microstructural mechanism responsible for fracture healing.

(continued)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☒ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL
DR S Wu

22b. TELEPHONE NUMBER *(Include Area Code)*
202-767-6962

22c. OFFICE SYMBOL
AFOSR/NA

DD FORM 1473, 83 APR

Rheo-optics and infrared analysis using a Fourier transport infrared spectrometer are being used to establish the microstructural composition of asphalt cements that influence or control the creep, relaxation and fracture healing processes. The FTIR analysis is being performed on a thin film of asphalt that is being sheared as the IR spectra is being recorded. This process allows spectral shifts to be studied as a means to determine which microstructural elements contribute to the processes of creep, relaxation and fracture healing. A microstructural model is being established which combines the dispersed polar fluid model, the modified Rouse model and the quantity and length of the linear appendages to the various molecules which comprise the asphalt microstructure. This microstructural model provides a reasonable explanation of the processes of creep, relaxation and fracture healing.

Additional work in the final year of this grant is discussed to complete the development and verification of the microstructural model.

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SUMMARY

All three research issues have been addressed during the first two years of this grant. Concisely stated these issues are: (1) establish the mechanism of chemical healing of microcracks within the process zone preceding the macrocrack, (2) define the mechanism of relaxation and creep in asphalt cement and (3) establish a formal tie between permanent strain in asphalt concrete and cyclic loading and the creep compliance function.

We remain confident that the methodology used to evaluate fracture healing in asphalt concrete successfully differentiates among asphalts of different chemistry and different compositional make up. This is based on the testing of nine asphalts selected as representing a wide and interesting range of chemistry and compositional make up. These nine asphalts were tested during the first year of this grant. In year two additional fracture healing testing has been accomplished with asphalts modified with polymers. These polymers include low density polyethylene (LDPE) and two forms of amorphous polyalphaolefins engineered for asphalt modification. Analysis of these data are now being completed. Additional fracture healing testing will be accomplished during year three of this grant with other manufactured asphalts.

We have developed a hypothetical model of healing in the asphalt. The chemical and compositional make up of the asphalts tested to date indicate that the model explains, reasonably well, the fracture healing potential of these asphalts. This gives us great confidence that a more detailed and viable model explaining the healing phenomenon will result from this grant

following study in year three. The present healing postulate relates the ability of microcracks in the asphalt to heal to the polar functional groups that develop interaction among the molecules and the substituent linear appendages to the aromatic and cyclic components. The amount and length of these appendages affect chemical healing in a significant and predictable manner.

The ability to monitor transmission FTIR spectral shifts while asphalt in thin films (similar to that in asphalt concrete mixtures) is stressed in a shearing mode is a substantial and significant breakthrough. Tests during year one of this grant demonstrate that the testing methodology which has evolved during this research can identify spectral shifts which, in turn, identify the molecular mechanisms responsible for creep and relaxation of virgin asphalts and polymer-modified asphalts. Further testing using this technique was performed during year two. The principal focus of the year two effort was that of developing a better understanding of the FTIR spectral shifts caused by shear stressing and rheo-optical properties of the asphalts.

The major developments during year two are a confirmation that the number and length of the linear substituents or chains attached to the various hydrocarbon components of the asphalt molecules affect the relaxation, creep and healing properties of the asphalt in a very significant and predictable manner. A close and careful review and evaluation of the state of the knowledge of the molecular model of asphalt cement as it has evolved during the extensive Strategic Highway Research Program (SHRP) research reveals that the most current SHRP model, the dispersed polar fluid model (DPF), is quite compatible with the findings in this study. In fact this research should be able to add significantly to the findings of SHRP researches in the critical areas of the explanation of creep, relaxation and fracture healing behavior. Findings in this research demonstrate that the DPF model is, by itself, inadequate to fully explain the physical responses of relaxation, creep and fracture healing. However, in concert, the DPF model, a modified form of the Rouse solution model and the explanation of the role of the linear substituents may provide a more complete and satisfactory explanation of these physical phenomena. It will be shown in this summary report that the number and length of the linear substituents attached to the various molecules, both aromatic and naphtenic, possess strong and significant correlations to healing index, average relaxation time, relaxation modulus and zero shear viscosity.

The ability to clearly differentiate among the spectral shifts due to stressing of a virgin asphalt (unmodified) and a polymer-modified asphalt is illustrative of the potential power of this technique to identify interactions between asphalt and polymers and how these interactions influence relaxation and deformation in modified asphalt systems.

In this study the ability to predict dynamic responses in asphalt concrete with acceptable accuracy by using a viscoelastic model has been demonstrated. These dynamic responses can be determined based on cyclic loading or creep compliance data. The results open the door to numerous applications to pavement performance predictive modeling from non-destructive test data. This particular aspect of the study was performed primarily in year one with some follow-on work in year two. The follow-on work in year two has primarily dealt with the application on the non-linear viscoelastic correspondence principle to dense-graded asphalt concrete mixtures. Demonstration of the application of the non-linear viscoelastic correspondence principle to dense-graded asphalt mixtures allows application of this principle to the study of the hysteretic behavior of asphalt concrete.

RESEARCH OBJECTIVES

This research addresses three issues. The first is to establish the mechanism by which chemical healing of microcracks within the process zone preceding the macrocrack occurs. The second and allied issue is to define the mechanism controlling the process of relaxation and creep deformation within the process zone. A third issue is to study the possibility of establishing a formal tie between permanent strain in asphalt concrete under cyclic loading and the creep compliance function.

A technique has been developed at Texas A&M University by which to measure fracture healing in asphalt concrete samples. This process allows one to separately analyze the time-dependent, viscoelastic effects on healing and those effects which are not related to mechanical time dependency but are related to chemical and diffusion effects. A prime objective of this research is to utilize this technique of evaluating healing and to determine the mechanisms of relaxation and chemical phenomena which contribute to fracture healing. Since chemical healing can be quantified, identification of the component or components of the asphalt cement microstructure that control chemical healing will be determined.

The microstructural components which control creep and relaxation responses are, we believe, tied to the mechanisms leading to frequency shifting and band distortions which can be detected using FTIR analysis of asphalts under conditions of stress and relaxation. These stress-induced frequency shifts will be interpreted in terms of changes in potential energy functions due to deformed primary carbon-carbon bonds, valence angles, torsion angles and nonbonded interactions. These molecular deformation processes (inter and intra-molecular) occurring during the creep and relaxation mode will be identified using dynamic infrared analysis.

Asphalt concrete is a member of the broad class of materials thought to obey micromechanical principles (composites). The applicability of the correspondence principle developed by Schapery (1984) is a basic premise in this assumption. Schapery's work demonstrated the applicability of this principle to account for time dependence of asphalt concrete. However, further questions remain. The first concerns the use of non-linear viscoelastic fracture mechanics in accordance with Schapery's work (1984), and the second concerns the use of La Place Transformation in describing the complex compliance of asphalt concrete under cyclic loading. This work has the potential to lead to a formal tie between the creep compliance function and the function describing permanent strain under cyclic loading.

To accomplish the research objectives which spring from the three research issues discussed above, six tasks have been identified. These tasks are: (1) Select Asphalts Representing a Wide Range in Chemical Composition and Physical Nature for Evaluation, (2) Develop Hypothetical Microstructural Mechanism to Explain the Role of Relaxation in the Fracture Process, (3) Study Use of the Correspondence Principle for Deriving the Complex Compliance of Asphalt Concrete Under Cyclic Loading, (4) Develop the Hypothetical Microstructural Mechanism to Explain the Role of Chemical Healing in the Fracture Process, (5) Perform Relaxation and Healing Testing of Asphalt Samples and (6) Produce Specific Asphalts by Supercritical Fractionation and Recombination for Verification of Healing and Relaxation Mechanisms.

STATUS OF THE RESEARCH

The status of the research will be presented in six sections coinciding with the six tasks to be accomplished in this research.

Task 1 - Selection of Asphalts

Fifteen asphalt cements have been selected for this study after a careful study of the asphalts available. These asphalts were selected because of their diversity of chemical and physical properties which might influence fracture healing and relaxation properties. Ten of the fifteen asphalts are from natural sources while three are manufactured asphalts. These manufactured asphalts will be produced at Texas A&M with the goal of providing selected chemical and physical properties deemed important to the mechanisms of healing and relaxation. The manufactured asphalts will be produced using a supercritical fractionation technique. The three manufactured asphalts may not be produced until testing and analysis of the naturally occurring asphalts is complete. Based on the information obtained from the natural asphalts, manufactured asphalts with specific engineered properties will be produced and tested to verify the mechanisms proposed to explain fracture healing and relaxation. Two additional manufactured asphalts will consist of one of the naturally occurring asphalts modified with polymers. Specifically, the modifiers selected are low density polyethylene, styrene butadiene styrene and amorphous polyalphaolefins.

A summary of the rheological and other pertinent properties of most of the 15 selected asphalts is presented as Appendix A of the first year annual report.

Task 2 - Develop Hypothetical Microstructural Mechanism to Explain the Role of Relaxation in the Fracture Process

Recent Developments in the Chemical Model of Asphalt

The Strategic Highway Research Program (SHRP) is spending approximately $50 million on the study of asphalt over a short five year period. A significant effort in the SHRP program is the development of the chemical and physical property tests that best identify the properties of the asphalt which can be used to predict performance. As part of this effort, SHRP has spent a concerted effort on the identification of chemical model that represents asphalt.

SHRP has essentially rejected the long-held theory of a micellar model which pictures asphalt as relatively large lumps of material in a sticky gel. The newly held SHRP view is that the asphalt is a network structure and that the network is held together by polar bonds developed by functional group appendages to the hydrocarbon molecules.

SHRP researchers refer to the model as the "dispersed polar fluid" model (DPF). This model pictures the asphalt as a continuous, three-dimensional association of polar molecules dispersed in a fluid of non-polar or relatively low polarity molecules. Functional groups attached to the hydrocarbon molecules provide the interactive bonding between hydrocarbon molecules. These functional groups generally contain one of the heteroatoms of oxygen, nitrogen, sulfur or the trace elements. Many of these polar functional groups behave as either acids or bases and are capable of forming dipolar, intermolecular bonds of varying strength with functional groups of the opposite polarity.

In the DPS model, the viscoelastic properties of the asphalt, and its response to load and temperature-induced stress result directly from the formation and breaking of bonds between the polar molecules. These secondary bonds make and break continuously and control the relative motion among the molecules.

At very low temperatures, the DPS model depicts the asphalt as responding to external stress by the overall bending (vibrational) characteristics of the carbon-carbon bonds in all its constituent molecules as well as by the intermolecular associations among polar molecules. This seems to account for correlations observed between the low-temperature rheological response of asphalts, and chemical factors, such as the range of molecular weights found in the non-polar chromatographic fractions and the gross distribution of mass between the polar and non-polar asphalt fractions. At the high-temperature end of the spectrum, the form and strength of the association of polar molecules is dictated by the balance between non-polar and polar molecules present.

SHRP has identified several points in which the micellar and the DPS model differ. First, the micellar model postulates that the asphalt is a colloidal system with particles of a dimension very large on a molecular scale, representing the agglomeration of many individual asphalt molecules. Conversely, the DPS model depicts the asphalt molecular structure as very small and much smaller than the size of micelles. The DPS models predicts no large-scale assemblages of molecules. Instead, the microstructure depends upon instantaneous bonding among the wide variety of polar molecules dispersed in the asphalt. SHRP NMR analysis has failed to find any large-scale assemblages.

The second way in which SHRP has identified a difference between the micellar model and the DPF model is that in the micellar model the colloidal particles are considered to be relatively permanent assemblages suspended in the dispersing medium. Conversely, the DPF model postulates that the continuous forming and reforming of the structure through energy flows to and from the media of external loading and temperature fluctuations.

Thirdly, the DPF model stresses the importance of the polar asphalt molecules in mediating performance to a larger degree than the micellar model. Western Research Institute (WRI) has used ion exchange chromatography (IEC) to separate molecules with polar functional groups, which act as fundamental units in the DPF microstructural model. In the IEC analysis, dissolved asphalt is filtered through ionically charged resin beads that will attract the polar materials. If the material is filtered through the negatively charged resin beads first, the cations will attract all the acid polar materials. A filtration of the remaining solution through positively charged resin beads would attract all basic polar materials. The twice filter solution would then contain only the neutral or non-polar material. WRI researchers are using this technique to reveal how the polar functional groups affect chemical and physical properties.

From the IEC analysis, WRI has identified a class of polar molecules, the amphoteric materials, as the group having the principal effect on the asphalt structure. These molecules have at least one negative and one positive charge in the same molecule and can extensively associate because they can fasten to other molecules at two or more sites instead of one.

The work in AFOSR-89-0520 concentrates on the microstructural mechanisms of relaxation and fracture healing. The approach to the understanding of these microstructural mechanisms is actually quite different than the approach to understanding the chemical structure of the asphalt. Although the intermolecular polar bonds may well control the structure of the asphalt, the question still remains as to how the asphalt microstructure behaves under loading. To the knowledge of the investigators in this study, AFOSR Grant 89-0520 remains the only study to investigate the changes in the microstructure of the asphalt under loading or stressing. The clear indication at this point in our analysis is that the abundance and lengths of the linear chains have a significant and perhaps dominant influence on the relaxation and deformation behavior of the asphalt. In additions the lengths of the linear chains significantly influence the relaxation time and the potential for the asphalt to chemically heal fracture surfaces. NMR studies clearly define that the linear hydrocarbon chains that influence the relaxation and fracture healing properties of the asphalt are attached to all of the "component" fractions of the asphalt (asphaltenes, polar aromatics and napthenic aromatics). The NMR analysis does not define the nature of the ends to which the chains are anchored and whether or not they consist of polar functional groups. The relationship between the SHRP DPF model and the work done on this study is quite compatible, and the interaction of these studies should shed considerable light on the microstructural nature of the asphalt and how this structure influences relaxation, deformation and fracture properties.

Developments in AFOSR-89-0520 in Year Two

The experimental focus of this research has been on rheological properties and analysis by infrared spectroscopy in addition to a rheo-optical technic that combines extensional rheology and infrared spectroscopy. Rheology offers a way of not only characterizing the thermo-mechanical properties of asphalt but of delineating issues of asphalt modification and compatibility, important structure characteristics that control mechanical properties and predictive tools for determining behavior at several temperatures and rates of deformation. Infrared spectroscopy provides a method for correlating molecular information with the thermo-mechanical characterization.

Most asphalts have been determined to be viscoelastic at all temperatures measured. The molecular origins of this observed behavior are questionable and can be probed by applying various molecular models to the interpretation of dynamic viscoelastic spectra. In particular, we have considered the application of the concentrated solution Rouse and modified Rosue models (Ferry et al., 1955). Results indicate that this may be a reasonable model to use for predicting mechanical properties.

A second model used to characterize viscoelastic properties is the star branched model. If one accepts Monismith's (1961) model of an asphalt molecule, it is clear that "branches" of aliphatic, aromatic and cyclic structures exist. One would expect these materials to behave similarly to star-branched polymer molecules (Pearson and Helfard, 1983). By comparing the behavior of the asphalts with those of star-branched molecules, qualitative information as to the structure/property relationships in these systems can extracted.

For both models outlined above, quantitative information can be used, and correlated with known behavior. In the work presented, the rheological properties used are the glass transition temperature, which is a measure of compatibility and changes in the molecular structure; the average relaxation time, which provides a measure of the strength of the viscoelastic process and its time dependence; effective molecular weight as calculated from rheological parameters; the loss modulus G" and the storage modulus G′, both providing information as to the ability of an asphalt to deform; and the viscoelastic shift factor a_T, that describes the temperature dependence of the relaxation process. The use of these parameters is presented in more detail, later in the text.

Rouse and Modified Rouse Models

The work of Gaskins et al. (1960) indicates that an asphalt can be modeled as a solution containing a viscoelastic solute. This description implies that the asphalt is but a macromolecular solution. Whether the macromolecule is an extended structure as in a polymer, or is a virtual structure as in colloidal systems, is still an issue to be resolved. However, the size of this structure is easily determined from the Rouse model parameters. The Rouse model in its mathematical form for the viscoelastic functions is presented below.

$$G' = nkT \sum_{p=1}^{N} \frac{w^2\tau_p^2}{(1 + w^2\tau_p^2)}$$

$$G'' = \sum_{p=1}^{N} \frac{w\tau_p^2}{(1 + w^2\tau_p^2)}$$

where

$\tau_p = f(M_n)$,

$nkT = \dfrac{CRT}{M}$,

m = molecular weight,

c = concentration,

R = gas constant,

K = Beltzman constant, and

T = temperature.

To predict the behavior of an asphalt, the effective molecular weight is determined. It is important to note that the zero shear viscosity and the molecular weight are the only adjustable parameters in this complex model. The zero shear viscosity being determined from experimental data, leaves only the molecular weight as an adjustable parameter. For the asphalts studied, the effective molecular weight is on the order of 10^3 to 10^4 grams/mole. Noting Monismith's (1961) model of linear structures branched from fused, aromatic rings, this value is in line with approximate molecular weights of structures he proposed. Coupled with the rheo-optical work described below, this data suggests that the model proposed by Monismith is a realistic description of the "form" of the asphalt structure and that the length of the linear segments controls, or is an important contributor, to the relaxation processes of asphalt. It is not clear from this information how the proposed model of asphaltenes and resins suspended in oil modifies the behavior of the asphalt molecule. A closer evaluation of the SHRP DFS model is required in this level of the investigation. Further work, utilizing x-ray scattering and light scattering techniques, in bulk and in solution, would help in characterizing this macrostructure but will also aid in determining the temperature stability of such structures. For several polyethylene modified asphalts, using molecular weights typical of commercial resins (10^6 grams/mole), the molecular weights are predicted to increase to values on the order of 10^5 to 10^6 grams/mole. This predicted increase is in agreement with the observed increase determined from the Rouse model. This further supports the suggestion that the branched linear model is appropriate for understanding the rheological behavior of most asphalts.

Star-Branch Models

The model of Pearson and Helfand (Macromolecules 1984) predicts the rheological behavior of a molecule in which the structure is similar to a star, several linear branches emanating from a central point. To some extent, the molecular topology offered by Monismith (1961) suggests the modeling of an asphalt molecule as a star branch structure. When fitting the asphalt rheological data to this model, there were several short comings that suggested that this model was inappropriate for representing the asphalt's behavior. The model predicts a terminal flow region as is observed in asphalts at high temperatures, but it does not reproduce the behavior observed shortly before the glass transition temperature. It is unclear as to why this occurs and can only be determined from further work which details more of the material's morphology. A detailed description of the star branch model is not provided here because of its complexity. The reader is referred to the original work of Pearson et al. (1983).

Rheo-optical Analysis

The strength of rheological modeling lies in its ability to predict the behavior of materials under various conditions, knowing the relaxation spectra and the temperature dependence from viscoelastic shift factors. In addition, the viscoelastic shift factors provide information into the origins and the energetics of molecular processes which control deformation at a given temperature. In order to successfully model materials in this fashion, an approximation to the relaxation spectrum (or retardation spectrum) must be determined from appropriate experimentation. To this end, dynamic mechanical experiments were conducted to measure the storage and loss shear moduli, G′ and G", respectively, over a frequency range of 0.1 radians/second to 100 radians/second. From this information, a master curve was constructed as detailed by Prapnnachari (1991). From this master curve, the relaxation spectrum was calculated using the methods of Baumgaertel and Winter (1989). Typical results are presented in Figures 1. The relaxation spectrum represents the distribution of the relaxation process (with their associated relaxation time) providing detailed information as to the weighing of relaxation times. From this spectra, the average relaxation time is determined as presented below.

$$\overline{\tau_w} = \frac{\int_{\infty}^{-\infty} \tau^2 H(\tau)\, d\ln\tau}{\int_{\infty}^{-\infty} \tau H(\tau)\, d\ln\tau}$$

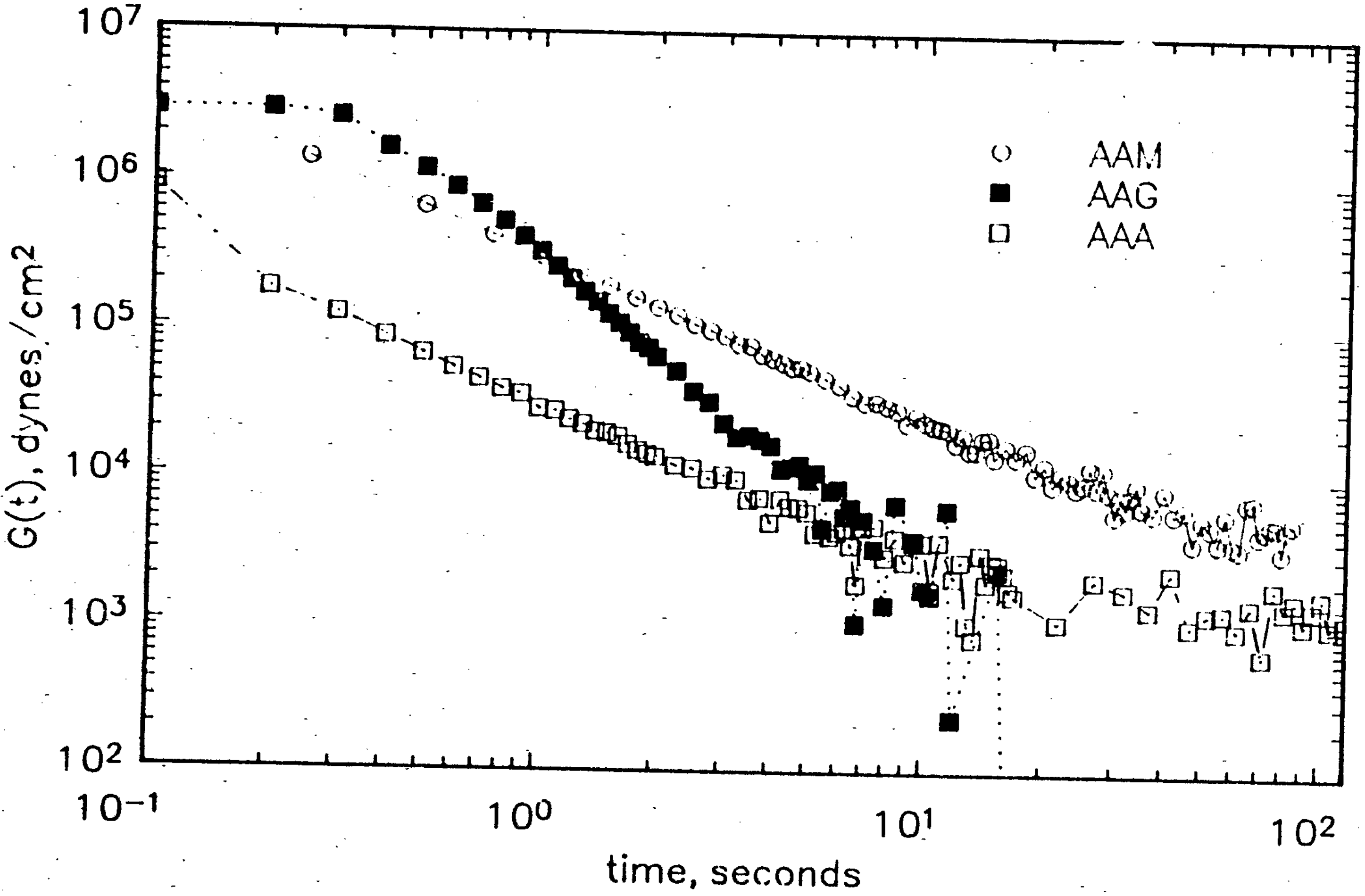

Figure 1. Master relaxation plots for asphalts AAA, AAG and AAM.

where

$\bar{\tau}_w$ = average relaxation time,

$H(\tau)$ = relaxation spectrum, and

τ = relaxation time.

The calculated average relaxation times were found to correlate well with an asphalt's healing index. For relative comparisons, the average relaxation time can be estimated as follows.

$$\tau_w = \frac{\int_{-\infty}^{\infty} t^2 G(t)\, d\ln t}{\int_{-\infty}^{\infty} t G(t)\, d\ln t}$$

For three SHRP asphalts, AAA, AAG, and AAM, the average relaxation times using the equation listed above were calculated to be 29.9 seconds, 0.8 seconds and 14.9 seconds, respectively. A comparison with the healing index presented in Figure 2, indicates a ranking based on the calculated relaxation times. Coupling this information with Infrared spectroscopy is intended to elucidate information as to the molecular origins of these relaxations.

The IR experimental setup includes two main units; a Nicolet model 60SXR IR Spectrometer and a Minimat materials tester manufactured by Polymer Laboratories Inc., Amherst, Massachusetts, that fits in the sample chamber of the spectrometer. The asphalt is deformed in shear between two NaCl plater. This mode of deformation while accommodating the sample holder of the Minimat, is also a realistic representation of how the asphalt is deformed in application and allows transmission of the IR beam through the sample. During testing the plates are deformed at an extensional rate of 6mm/minute. The size of the NaCl plate was 29 mm x 14 mm x 4 mm. To

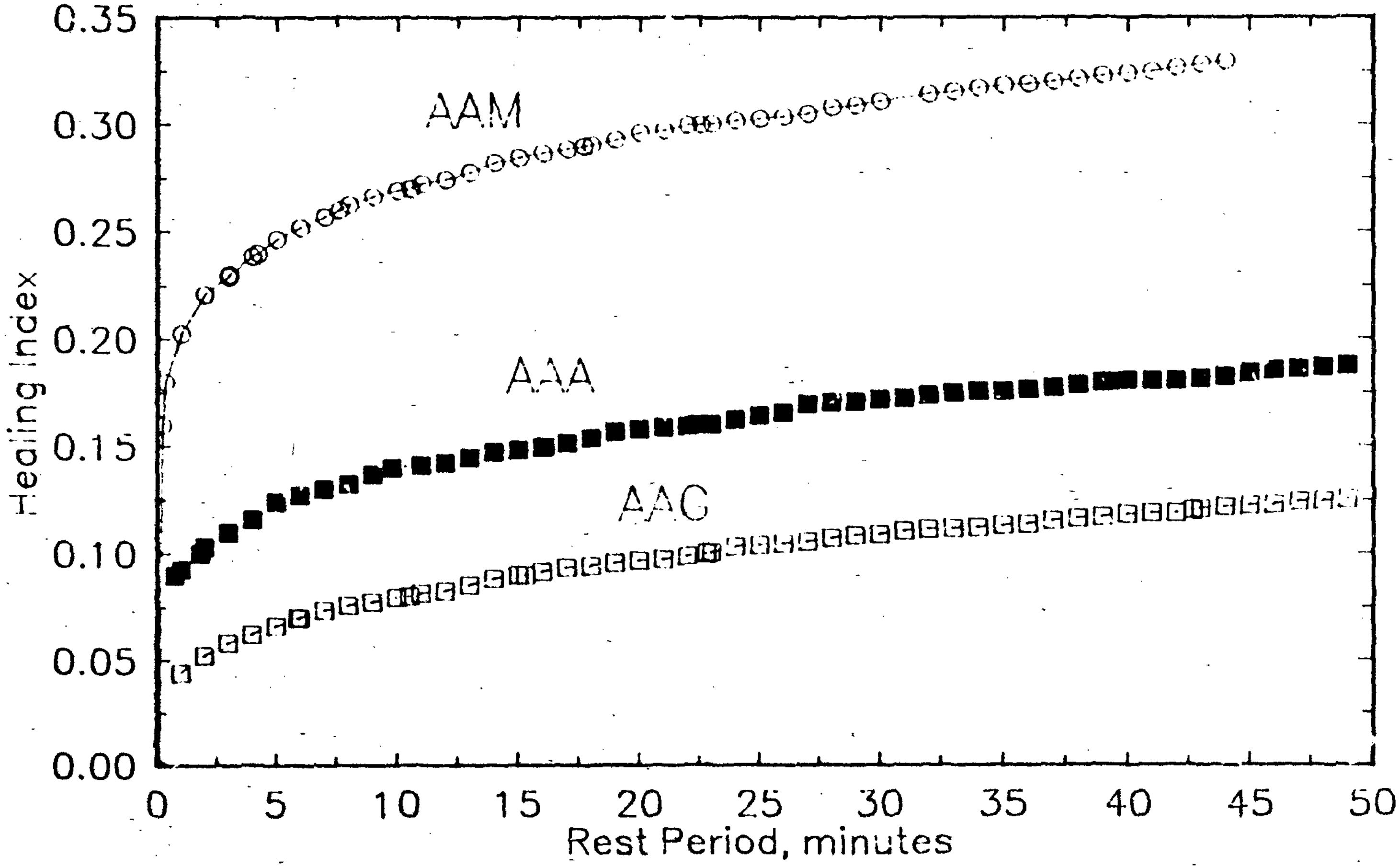

Figure 2. Healing index plots for asphalts AAA, AAG and AAM.

prepare a specimen, a film of asphalt is placed between two NaCL plates. One end of each plate is clamped to the Minimat test frame. In order to insure good contact between the plates and the asphalt, a small quantity of asphalt was smeared over a face of a NaCl plate at about 140 to 200°F. The second NaCl plate is pressed firmly by hand over the pre-treated NaCl plate. The resulting assembly is clamped into the sample holder. The portion of the plates exposed to the clamps is kept free of any asphalt.

A few comments on band assignments is in order to aid in data interpretation. Aromatic structures in a hydrocarbon can be found (Lambart et al. 1987) in five regions of the IR spectrum; 3100-3000 cm^1 for CH stretching, 1650-1430 cm^1 for C = C stretching, 1275-1000 cm^1 for inplane CH bending, 900-690 cm^1 for out-of-plane CH bending, and 2000-1700 cm^1 for overtones and combinations. In the IR spectrum of asphalts, weak absorbance near 1600 cm^{-1} suggests C=C stretching of the aromatics and small absorbance at 863, 813, and 745 cm^{-1} are for CH out-of-plane bending. The overtones and in-plane CH bending were not witnessed.

The region near 1460 and 1375 cm^1 reveals the presence of methylene and methyl groups. The band near 1460 cm^1 indicates the antisymmetric deformation of HCH angle of a CH_3 molecule. The bending of methylene (CH_2) groups also gives rise to a band in the same region. The symmetric CH_3 bending gives a strong, sharp band near 1376 cm^1. A small band near 720 cm^1 is indicative of a linear chain containing four or more CH_2 groups. The relative numbers of CH_2 and CH_3 groups are evaluated by the combined study of the 1460, 1376, and 720 cm^1 bands. When there are more CH_2 groups than CH_3 groups present, the 1460 cm^1 band will be stronger (Lambart et al. 1987) than the 1376 cm^1 band. The greater relative intensity of the band near 1460 cm^1 than 1376 cm^1 is found in general in IR spectrum of all the asphalts. This suggests the dominance of CH_2 groups over CH_3 groups in the asphalt molecules. The relative length of CH_2 chains among asphalts can be evaluated by the study of the 720 cm^{-1} band.

By comparing the ratio of several bands to internal references, the effect of specimen thinning is differentiated from the effect of molecular structure. After comparing appropriate absorbance bands, it was determined that the 721 cm^{-1} absorbance band was the peak most related to the deformation process, suggesting that the chain length associated with the asphalt molecule is key in determining mechanical properties. This is reviewed in more detail below.

Rheo-optical Results

Observed spectra changes occurred in the peak ratio of the CH2 and CH3 bands (721, 1376, and 1457 cm^1). The shearing of the asphalt sample in the IR beam indicated that the methylene structures, irrespective of their position in the molecule, were actively involved with the applied stress. The band at 721 cm^1 is for skeletal rocking of CH_2 molecules while the band at 1376 cm^1 represents the symmetrical bending mode vibration of CH_3 molecules; the band at 1457 cm^1 presents the combined symmetrical and asymmetrical bending modes for CH_2 and CH_3 molecules.

The length of an alipnatic branch is represented by the CH_2 to CH_3 ratio, the higher the ratio, the longer the chain. These ratios are proportional to the ratios of the absorbance peaks associated with each unit. During shear deformation, the CH_2/CH_3 peak ratio is observed to change. This is only a qualitative indication of the structures involved in the deformation process but not an indication of the way in which they are involved. Since the asphalt film is thinning during the shearing process, it is difficult to make quantitative assements (measurement of band shifts, change in concentration, etc.), although qualitative assessments are valid since all other peak ratios are constant during deformation.

The results of the rheooptical analysis presented above, suggests a relationship between the linear structures and the mechanical properties of the asphalt. To test this hypothesis, the relaxation properties of the asphalts are compared with the ratio of the average relaxation time and the zero shear viscosity. The zero shear viscosity is related to the average relaxation time. Its relationship to the relaxation modulus is seen in the equation presented below.

$$\eta_0 = \int_{-\infty}^{\infty} tG(t)\,d\ln\tau$$

In Figure 3, a strong correlation is observed between the zero shear viscosity and the ratio of the absorbance peaks, 721 cm^{-1} and 1376 cm^{-1}. This result suggests a strong correlation between linear "structures" and the relaxational process of the bulk asphalt.

Task 3 - Study Use of Correspondence Principle for Deriving the Complex Compliance of Asphalt Concrete Under Cyclic Loading

Research Activities at NCSU

The objective of the subcontract at North Carolina State University

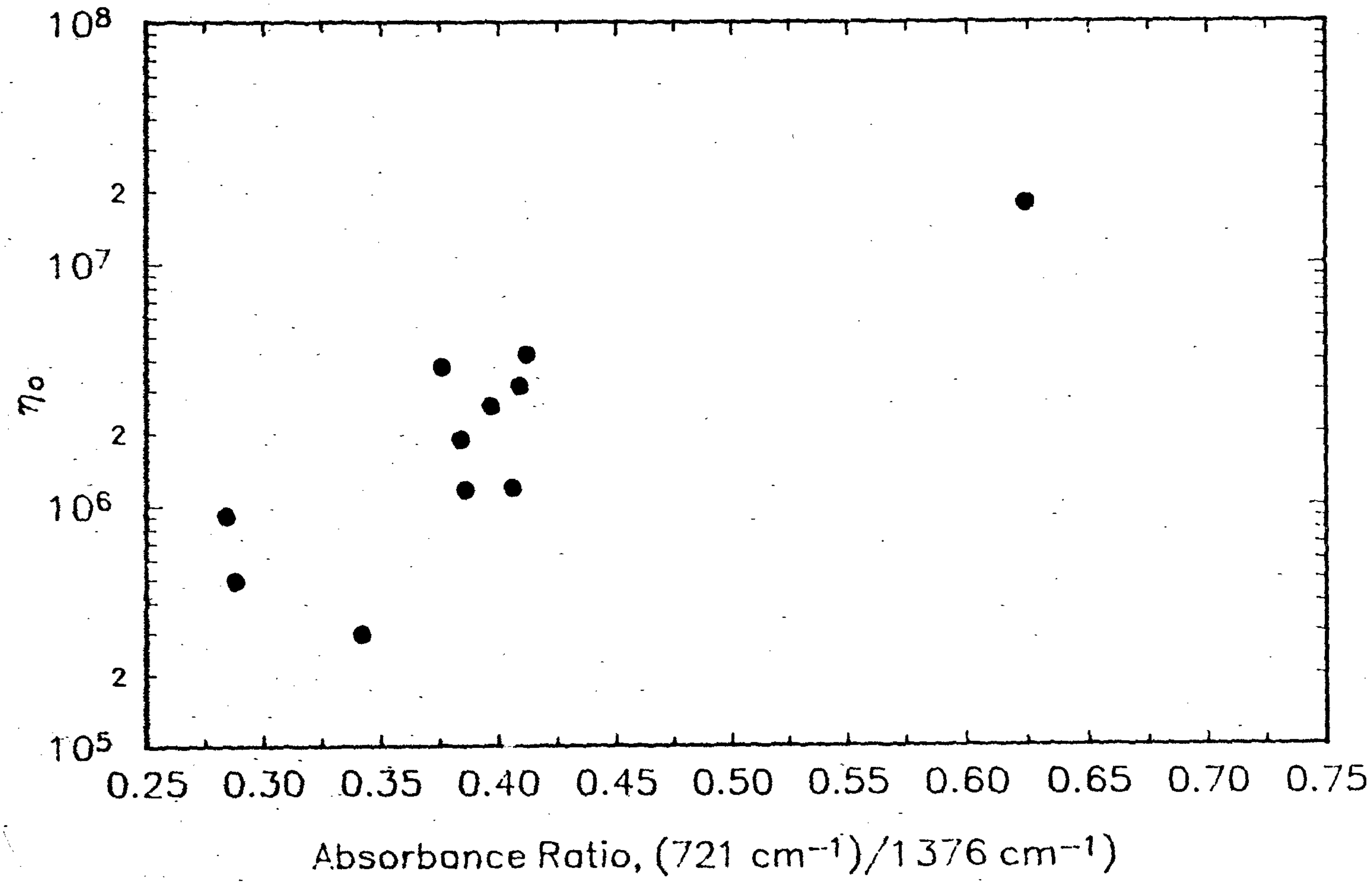

Figure 3. Correlation between zero shear viscosity and the ratio of absorbance peaks 721 cm^{-1} and 1376 cm^{-1}.

(NCSU) is to validate the applicability of the nonlinear viscoelastic correspondence principle to controlled-stress and controlled-strain uniaxial cyclic testing data on realistic dense-graded asphalt mixtures. the materials selected for this study include Watsonville granite aggregates and California Valley AR-4000 graded asphalt cement. Cylindrical specimens with 4-inch diameter and 8-inch height were fabricated by COE Gyratory Testing Machine. The sample preparation protocol recommended by the Strategic Highway Research Program A-003A was followed in this study.

Application of both the pseudo stresses and pseudo strains developed by Schapery are under consideration for the controlled-stress and controlled-strain tests, respectively. The pseudo stresses and pseudo strains can be determined from the following:

$$\sigma_{\bar{y}}{}^{E} = E_R \int_0^t D(t - \tau) \frac{d\sigma_{\bar{y}}}{d\tau} d\tau \tag{1}$$

$$\epsilon_{\bar{y}}{}^{R} = \frac{1}{E_R} \int_0^t E(t - \tau) \frac{d\epsilon_{\bar{y}}}{d\tau} d\tau \tag{2}$$

where

$\sigma_{\bar{y}}$, $\epsilon_{\bar{y}}$ = stresses and strains,

$\sigma_{\bar{y}}{}^{R}$, $\epsilon_{\bar{y}}{}^{R}$ = pseudo stresses and pseudo strains,

E(t), D(t) = relaxation modulus and creep compliance as a function of time, and

E_R = reference modulus which is an arbitrary constant.

In order to determine the fundamental properties needed in the calculation of pseudo stress and pseudo strains, uniaxial compressive creep tests and relaxation tests were performed on the cylindrical specimens at 0, 32, 50, 73, and 104°F. The levels of constant load and constant displacement used in the creep tests and relaxation tests respectively were kept relatively small not to induce significant damage during testing. Plots of relaxation modulus or creep compliance versus time in a logarithmic scale were generated. The horizontal shift of the creep curves and relaxation curves revealed that the asphalt mixture investigated in this study behaves "thermorheologically simple." This implies that the master creep or relaxation curves can be constructed by shifting individual creep or relaxation curves horizontally.

A data acquisition and analysis program for the repetitive testing is currently under development. The cyclic data obtained from this program and the concept of pseudo stresses and strains will be used in validating the application of the nonlinear viscoelastic correspondence principle to studying the hysteretic behavior of asphalt concrete.

The result of this study will be imported in detail in the final report.

Task 4 - Develop Hypothetical Microstructural Mechanism to Explain the Role of Chemical Healing in the Fracture Process

This task directly addresses one of the major research issues of this study. It is important to develop a "working' hypothesis of the healing mechanism. This model has been developed and is based on the following input: (1) published literature, (2) chemistry, asphalt rheology and mechanics of asphalt concrete behavior and (3) research (chemical and rheological) from the SHRP research program: contracts A-002a, A-002b, A-002c, A-003a, A-003b, AIIR projects supplementary to A-003a and A-005.

Probably the most valuable source of information used in developing a "working" hypothetical model has been from meetings, written communications and telephone conversations with the following experts: Dr. Claine Petersen, Dr. Jan Branthaver, Dr. Keith Ensley, Mr. Henry Plancher, Dr. Wynn Jennings, Dr. Alan Letton, Dr. Murray Jelling, Dr. Christine Curtis, Dr. Carl Monismith, Dr. Ron Terrel, Dr. Dick Davisson, Dr. Ray Roberton, Mr. Vyt Pusinauskas, Dr. David Anderson and Mr. Joe Button.

The working model of the asphalt at this point is different from that discussed in the first year annual report. This model combines the DFS model and the Rouse solution model explained under the discussion of Task 2. For a complete and satisfactory presentation of this model, we believe it is necessary to include the influence of the linear substituent chain appendages as they have been proven to relate to relaxation, creep and fracture healing in a significant and predicable manner.

Based on the twelve asphalts tested for fracture healing properties and the chemical and analytical data collected and measured on these asphalts, several parameters have been identified as most important to the healing mechanism. These include: the solvency power of the neutral fraction, the percentage of the neutral fraction, the chemical structure of the neutral fraction, the acid/base ratio, the level of dispersion of the asphalt (the Heithaus parameter is an excellent measure of dispersion), the asphalt compatibility ratio, the aliphatic structure within various generic fractions as determined by NMR and the number of carbon, hydrogen, sulfur, oxygen and nitrogen atoms present in the aromatic and aliphatic fractions of the asphalt (as determined by NMR).

The work underway and proposal in year three will shed substantial light on this research issue.

Task 5 - Relaxation and Healing Testing of Asphalt Samples

Fracture healing tests are being performed on twelve naturally occurring asphalts. Eight of the naturally occurring asphalts have been tested for fracture healing potential as a part of SHRP contract A-002a. Replicate samples of these same asphalts were also tested in this study with the addition of the Santa Maria asphalt with and without modification with polyethylene. Three replicate samples were tested for each phase of testing: relaxation modulus determination, pseudo strain verification phase and healing phase. Three additional asphalts with atactic polypropylene modification were also tested.

Considerable and detailed rheological testing has been performed on the eight core SHRP asphalts and four additional asphalts, each with and without polymer modification (two with LDPE modification and two with amorphous polyalphaolefin modification). Rheological testing is discussed in Task 2 in a summary form and again in Appendix A. A more detailed discussion will follow as discussed in the section entitled "Publications Resulting from This Research."

Task 6 - Produce Specific Asphalts by Supercritical Fractionation and Recombination for Verification

This task will begin in year three.

PUBLICATIONS RESULTING FROM THIS RESEARCH

Following the findings of year two the following publications are either underway or are planned:

1. "Investigation of the Microstructural Mechanism of Relaxation in

Asphalt," Ph.D. Dissertation, Srikrishna Prapnnachari, December, 1991. This publication is complete and is being edited by D. N. Little. The report will be submitted by AFOSR as an addendum to the annual report by December 20, 1991. The report is 250 pages in length.

2. "Materials Characterization of Asphalt and Polyer-Modified Asphalt," Master of Science Thesis, Mohan Paramasivam, December, 1991. This publication is complete and is being edited by Drs. Allen Letton and D. N. Little. The report will be submitted to AFOSR as an addendum to the annual report by December 20, 1991. The report is 99 pages in length.

3. "Use of Fouier Transformed IR Spectral Shifts During Stressing to Identify Mechanisms of Reinforcement in Polymer-Modified Asphalt," Transportation Research Record, Prapnnachari, P. and Little, D. N., July, 1992 (planned).

4. "Proposed Mechanism of Stress Relaxation and Resistance to Deformation in Thin Films of Asphalt Cement," Materials Journal of ASCE, Little, D. N. and Prapnnachari, P., July, 1992 (planned).

5. "Identification of the Mechanism of Modification of Asphalt Cements with Low Density Polyethylene," Journal of Association of Asphalt Paving Technologists, Little, D. N., Prapnnachari, P. and Letton, A., August, 1992 (planned).

6. "Mechanism of Fracture Healing in Asphalt Concrete," Journal of Materials, ASCE, Prapnnachari, P., Little, D. N., Kim, R. and Puzinauskas, V., January, 1992 (planned).

7. "Improvement of Fracture Healing Potential of Asphalt Cements through Polymer Modification," Journal of Association of Asphalt Paving Technologists, Little, D. N., Kim, R., Shuler, S. and Letton, A., August,

1992 (planned).

8. "Use of Basic Viscoelastic Functions to Establish Formal Tie Between Permanent Strain in Asphalt Concrete Under Cyclic Loading and the Creep Compliance Function," Engineering Mechanics Journal of ASCE, Magnuson, A., Lytton, R. L and Little, D. N., January, 1992 (planned).

9. "Prediction of Hysteretic Behavior of Asphalt Concrete Based on Nonlinear Viscoelastic Correspondence Principle," Kim and Little, ASCE (1992, proposed).

PARTICIPATING PROFESSIONALS

Below are listed the professionals participating and associated with this research:

Professional	Affiliation	Role
D. N. Little	Texas A&M	Prin. invest.
R. L. Lytton	Texas A&M	Researcher
P. Prapnnachari	Texas A&M	Ph.D. student
A. Letton	Texas A&M	FTIR/rheology consultant
R. Schapery	Texas A&M	General consultant
A. Magnuson	Texas A&M	Researcher
R. Robertson	Wester Research Institute (WRI)	Interested party
J. Branthaver	WRI	Interested party
C. Petersen	WRI	Interested party
K. Ensley	WRI	Interested party

W. Jennings	Montana State Univ.	Interested party
S. Shuler	Asphalt Institute	Consultant
V. Puzinauskas	Asphalt Institute	Consultant
D. Anderson	Penn State Univ.	Interested party
R. Kim	North Carolina State Univ.	Consultant
F. Benson	Engitech, Inc.	Consultant

PRINCIPAL ACTIVITIES PLANNED FOR 1991-1992

General Overview

Our future efforts are focused at delineating the specific nature of asphalt structures, and the prediction of appropriate rheological properties based on these structures. To this end, we will focus on two characterization tools that lend themselves to solving these problems: x-ray scattering and controlled rheological studies. Using these tools a more in depth understanding of an asphalt's structure can be determined. Specific research efforts are presented below in more detail. X-ray diffraction facilities as well as rheological characterization tools are currently available in our laboratories.

X-ray Scattering Study of Various Asphalts

It is clear that the Corbett fractions vary for different asphalts, varying by refinery and by viscosity. Extensive efforts have been made to measure and identify the various fractions with little work pointed at understanding the particular interactions between these fractions. Our efforts will utilize wide angle and small angle x-ray scattering to determine characteristic distances and lengths for the asphalt structure. From wide angle x-ray scattering corrected intensities one can calculate, through the use of appropriate transforms, the radial distribution function for the scattering material. This distribution function identifies the interaction distances characteristic of a particular system. An example is provide for an assembly of spheres with an average radius of 2.65 angstroms. You will note in Figure 4 that a sharp rise in the radial distribution function is noted at 5.3 angstroms, associated with the closest distance of two spheres. Additional peaks are evident at distances that are multiples of the 5.3

angstrom distance. Although this data represents uniform, randomly packed spheres, a similar analysis will provide information as to the size and distribution of any associations in an asphalt as long as those associations result in differences in electron density. X-ray data will be collected as a function of temperature to determine the changes in structure which can be correlated with the observed rheological changes.

After characterization of the base asphalts, polymers will be added and studied in the same fashion. In this study however, well characterized polymers will be used. Molecular weights ranging from 10^2 grams/mole to 10^7 grams/mole will be used. Although polyethylene is known to be incompatible with most asphalts, no determination as to the nature of this incompatibility has been initiated in a systematic way. It is well known from polymer physics, that a trade-off between the entropic properties of polymer blends and enthalpic properties control blend compatibility. More specifically, the enthalpic contribution is most important since the entropic changes are negligible.

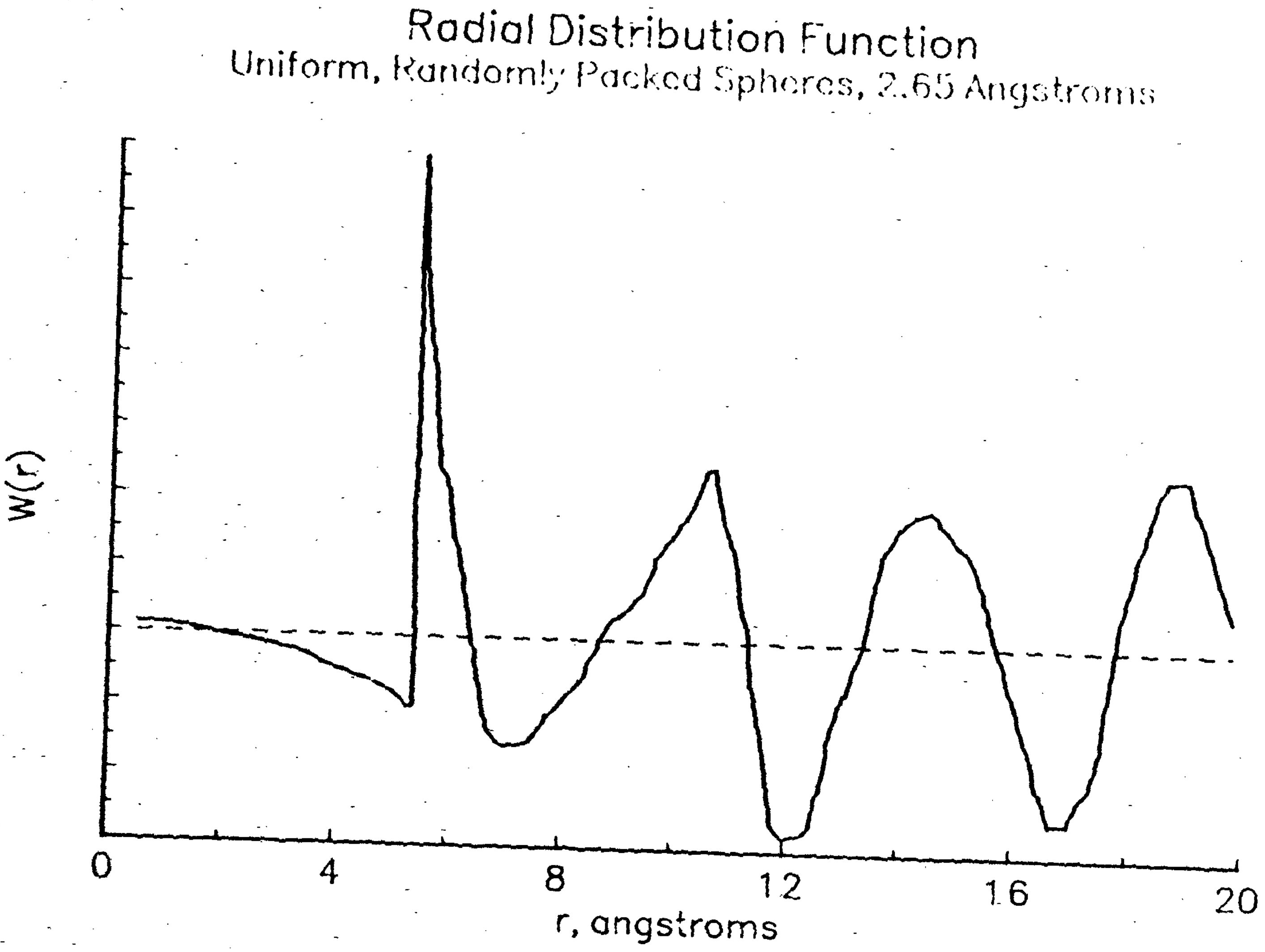

Figure 4. Radial distribution function of randomly packed spheres.

Normally, in polymer blends the enthalpic contribution dominates. For blends of polymers and asphalts, the entropic contribution can be controlled by varying the length of the polymer chain. In addition, by characterization of the various asphalt fractions, the enthalpic contribution can be determined (albeit in a qualitative manner) by knowing the relative ratios of the non-polar fractions, the polar fractions, saturates, etc. In this fashion, the important aspects of polymer/asphalt interactions are determined. The structure of asphalts is thereby determined indirectly. A strong entropic effect in the compatibility, as measured by changes in the glass transition for instance, will be evident when the molecular weight is changed. Such a change would indicate interactions with linear structures since the nature of the interactions is unchanged by changing the molecular weight, and the origins of rheological modification is known and can be used to better design the system. By varying the concentration of polymer, and polymer molecular weight, details of the interaction strength (through the Flory-Huggins interaction parameter [Paul J. Flory, "Principles of Polymer Chemistry", Cornell University Press, 1953]) are determined.

Rheology Studies

In addition to rheology studies mentioned above, current efforts suggest that a modified Rouse theory is appropriate for predicting the viscoelastic properties of asphalts. Such a model would not only provide insight into the structure of asphalt systems, but would be useful in developing a constitutive model that predicts the long term and processing properties of the asphalt. To further evaluate the modified Rouse theory, solutions of asphalt in several solvents, one being a theta solvent, will be studied in dilute solution regime. The viscoelastic information measured for the solution can be compared with model predictions for linear structures and colloid structures. Specifically, in the high frequency regime, for linear structures in the dilute solution the storage and loss moduli are expected to be parallel, not demonstrating the properties of highly interactive molecules. As the solution becomes more concentrated, and the asphalt takes its preferred conformation, a gradual approach to this conformation will be observed. By using solvent with different solubilities, information on the nature of these interactions can be extracted.

In addition to the rheological experiments presented above, experiments at low shear stresses are to be measured to determine the yielding nature of modified and unmodified asphalt. The proposed micelle structure for polymers is easily observed using a shear stress rheometer. The shear stress is slowly increased until yield is detected. Linear structures with weak interactions have little to no measurable yield stress where as micelle structures or structures with other interactions have significant yield stresses. Examples of this behavior are presented in Figure 5.

APPENDIX A

EVALUATION OF THE RELAXATION MECHANISM

Changes in the molecular structure of asphalts were observed in the collective IR absorbance spectra of asphalts subjected to shearing deformation. The perturbations and shoulders at random frequencies of the IR spectral region representing substituents to the aromatics are indicative

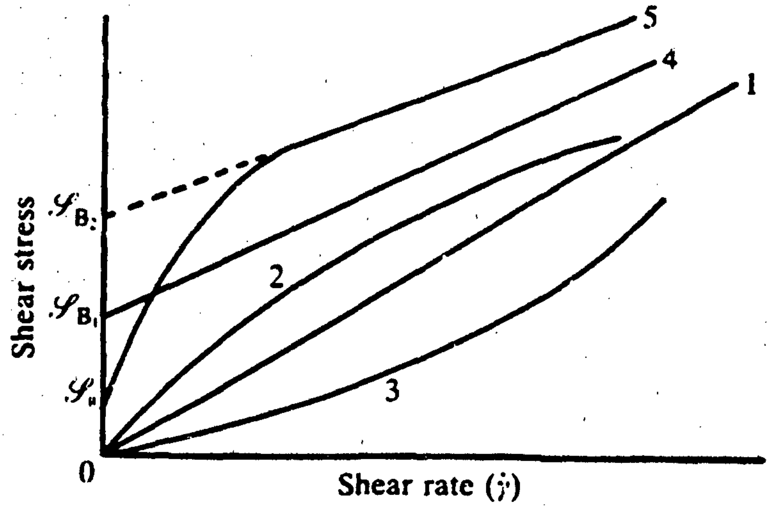

Figure 5. Flow behavior of micell or colloidal systems: (1) Newtonian, (2) shear thinning, (3) shear thickening, (4) Bingham plastic, (5) non-ideal Bingham plastic (Adapted from Foundations of Colloid Science, R. J. Hunter, Clarendon Pres, Oxford, 1987).

of the conformational changes to the appendages of the aromatics. Figure A.1 is an example for one of the 12 natural asphalts that demonstrates that most changes occurred in the peak ratio of CH_2 and CH_3 bands (721, 1376 and 1457 cm^{-1}). The shear deformation of the asphalt sample in the IR beam indicated that the methylene structures, irrespective of their position in the molecule, were most active in resisting the mechanical shearing stress. The band at 721 cm^{-1} is for skeletal rocking of CH_2 molecules. The band at 1376 cm^{-1} represents the symmetrical bending mode vibration of CH_3 molecules. The band at 1457 cm^{-1} represents the combined symmetrical and asymmetrical bending modes of vibration of CH_2 and CH_3 molecules, respectively.

The length of a methylene chain structure is represented by the ratio of CH_2 and CH_3 molecules present. The higher the ratio, the larger is the representative chain length. The changes observed in the ratio of the peaks of the absorbance bands offered qualitative information only. No fixed pattern of reproducability was observed for each stage of shearing deformation on replicates of the asphalt samples. Random changes in the peak ratio which indicates high randomness in the orientation and length of the asphalt chains was discovered. The representative data presented in Figures A.1, A.2, and A.3 suggests that the changes under mechanical stress were due bending and vibrations in the methyl and methylene molecules. The extent of changes could not be quantified because the asphalts possess significant random orientation of the short methylene chains. The representative chain length of the asphalt molecule represented by the ratio of CH_2 (721 cm^{-1}) to CH_3 (1376 cm^{-1}) absorbance of the unstretched or unsheared sample is compiled in Table A.1.

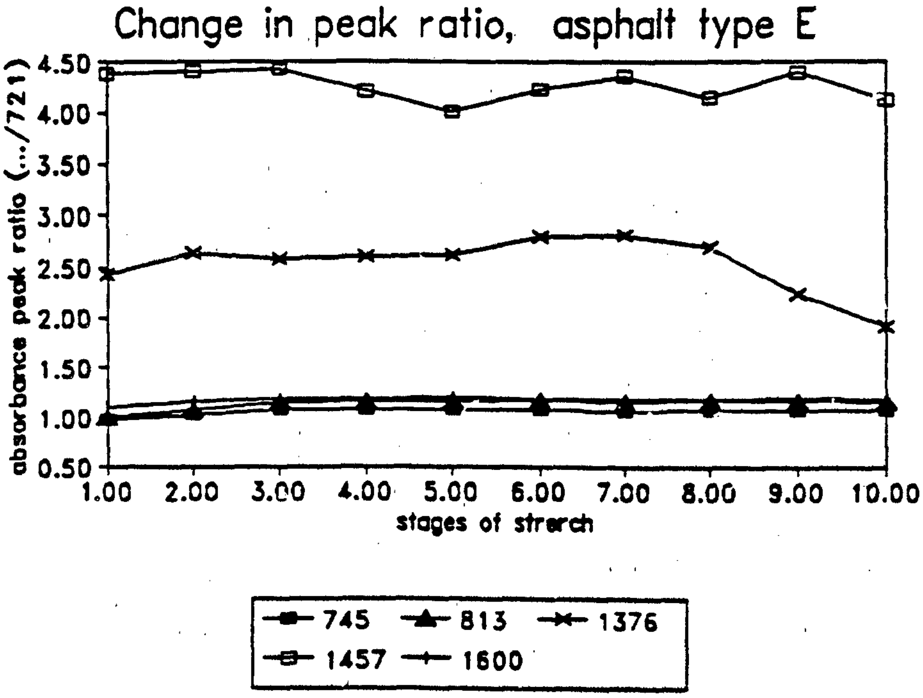

Figure A.1. Plot of peak ratio vs. shear stress stages for asphalt type E (one of 15 asphalts evaluated in this manner).

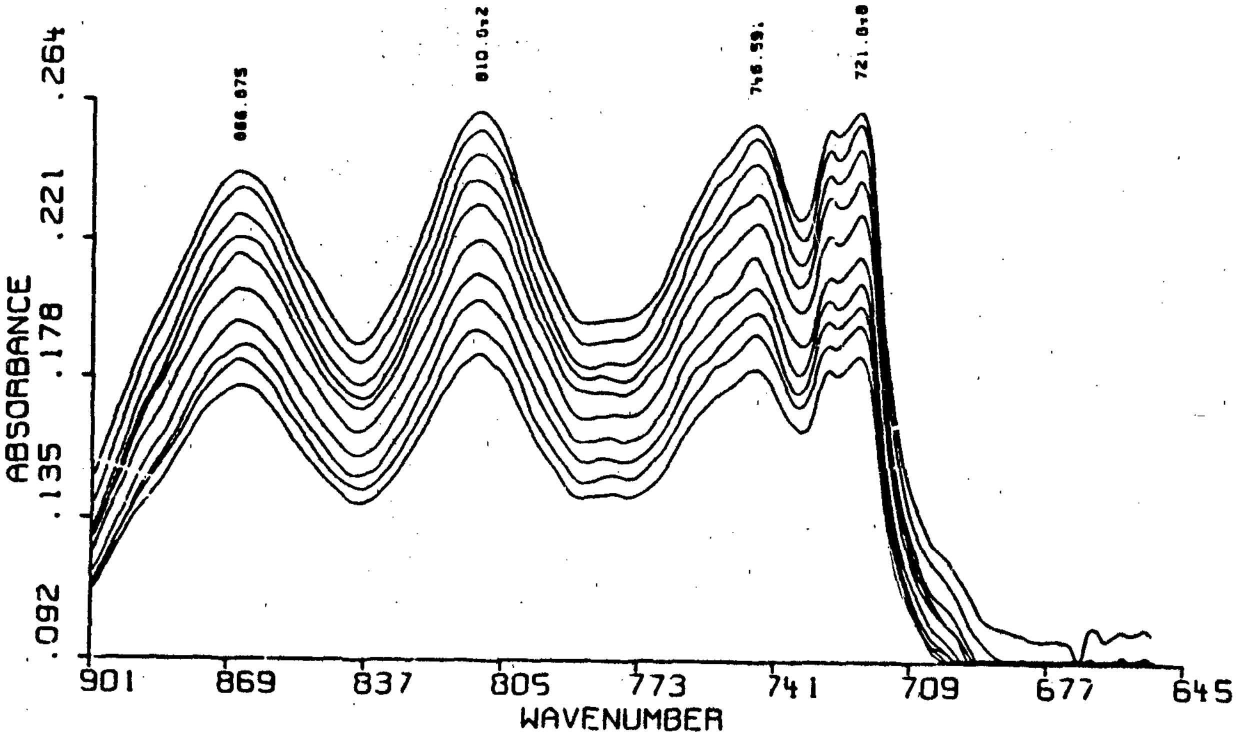

Figure A.2. Collective IR absorbance spectra (680-930 cm^{-1}) for the stages of shearing for asphalt E (one of 15 asphalt evaluated in this manner).

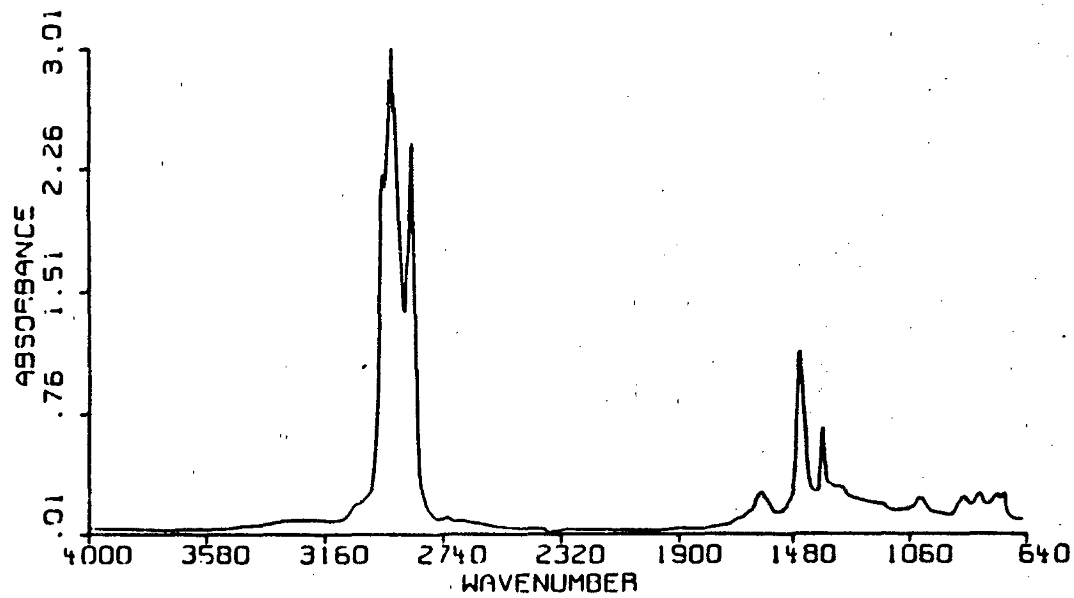

Figure A.3. IR absorbance spectrum (650-4000 cm^{-1}) for unstretched asphalt E (one of 15 asphalts evaluated in this manner).

Table A.1. The values of the ratio of peak absorbance of CH_2 (721 cm^{-1}) and CH_3 (1376 cm^{-1}), and the relaxation strength of the asphalts.

Asphalt type	Ratio of CH_2 (721 cm^{-1}) and CH_3 (1376 cm^{-1}) absorbance	Zero shear viscosity (poise)	Relaxation strength (dyn/cm^2)
A	0.342	2.95e+05	2.36e+06
B	0.284	9.16e+05	1.31e+07
C	0.624	1.78e+07	1.35e+08
D	0.409	3.14e+06	1.66e+07
E	0.412	4.23e+06	2.68e+07
F	0.386	1.17e+06	7.60e+06
G	0.406	1.19e+06	6.30e+06
H	0.397	2.59e+06	1.09e+07
I	0.384	1.89e+06	9.12e+06
J	0.288	4.90e+05	2.28e+06
K	0.376	3.76e+06	1.33e+07

The strength of the asphalt was evaluated by the relaxation spectrum obtained from the master curves of the storage and loss moduli. The master curves were constructed based on analysis of the dynamic mechanical test data. The experiment was carried out over the temperature range of from -25°C to 65°C, and the master curves, Figures A.4 was constructed at 25°C reference temperature. The absence of the rubbery plateau in the master curve of the asphalts suggests a single relaxation transition for the asphalts. This indicates that the asphalts basically possess polymeric solution type behavior.

Figures A.5 and A.6 exhibit the dependence of the relaxation strength of the asphalts on their representative chain length. The slope of the log viscosity and log relaxation strength versus CH_2/CH_3 plots are 4.2 with considerable scatter among the data. In the reputation model of polymeric solutions this slope is 3.45 with almost no scatter of data. This suggests that the asphalts lack true similarity with the polymeric solutions. The polymer solution models are indeed for high-molecular-weight chains. The asphalts are low-molecular-weight hydrocarbons and, therefore, the polymer solution models do not truly apply. However, the dependence of the relaxation behavior of the asphalts on the length of the chains is clear has been well established in this research. The deviation form the polymer solutions indicates that the asphalts are influenced by dispersed polar structure also. This is in agreement with the DPF structure proposed by SHRP.

The analysis of the generic fractions of the asphalts with relaxation parameters (relaxation strength and zero shear viscosity) did not show any significant correlations. It suggests that no component or the Corbett

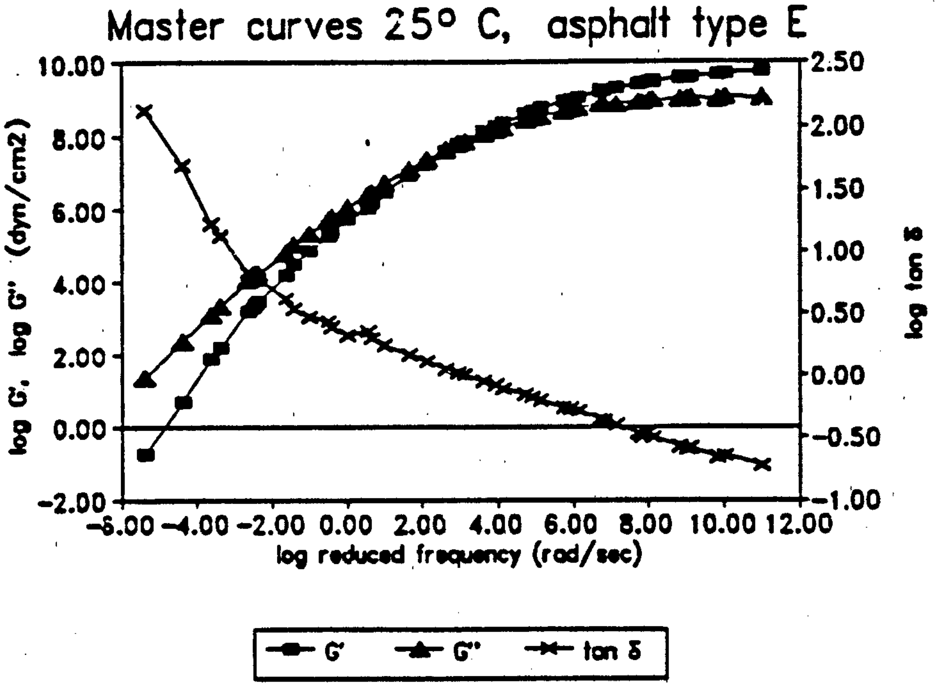

Figure A.4. Master curves of G′, G", and tan δ at 25°C asphalt E (one of 15 asphalts evaluated in this manner).

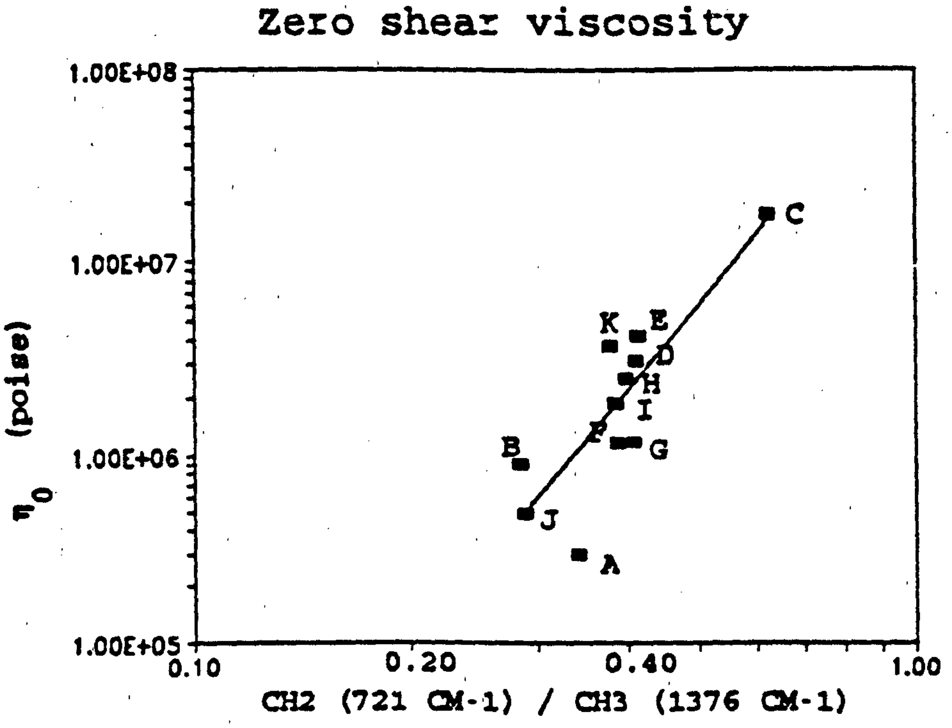

Figure A.5. Dependence of zero shear viscosity on length of the linear chains.

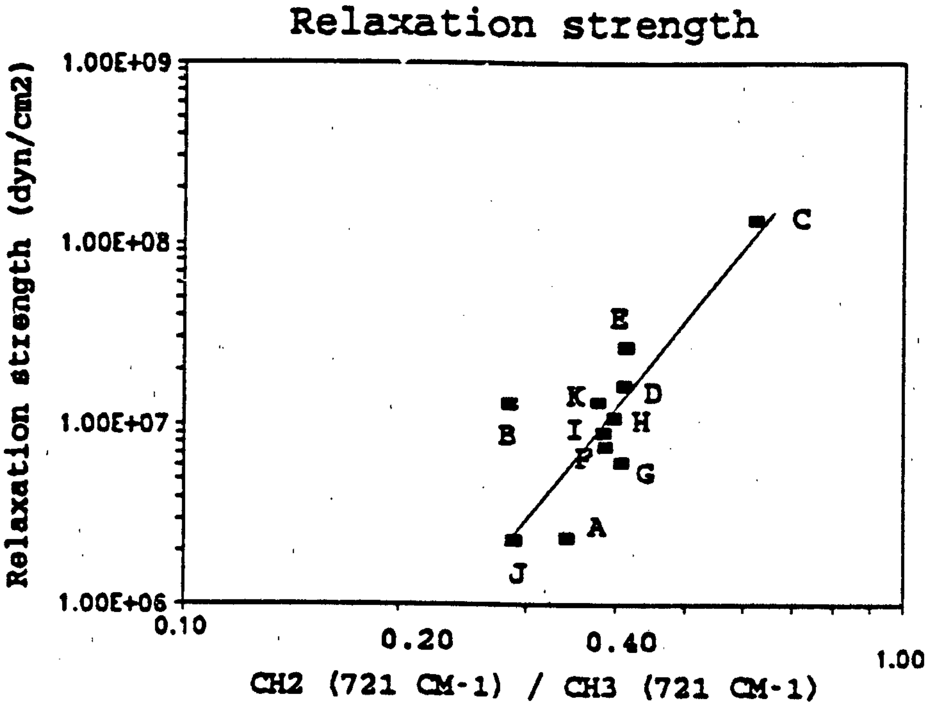

Figure A.6. Dependance of relaxation strength on the length of the linear chains.

fractions can, by itself, explain the physical property of the asphalts. A plot of the unrelaxed modulus of the asphalts shown in Figure A.7 demonstrate correlation (except for asphalt J) with their representative chain length. The long-term behavior observed through steady shear viscosity shows dependence on the chain-length. Asphalt type J, although it has an abnormally high initial modulus, does not maintain the long-term resistance against flow. Its initial high modulus might be due to highly polar interactions. Asphalt J has the highest asphaltene percentage, but since asphalt J has the smallest representative methylene chain length it lacks the long-term potential of resistance against flow. It may be therefore concluded that the methylene chains play a key role in promoting the component compatibility of the asphalts.

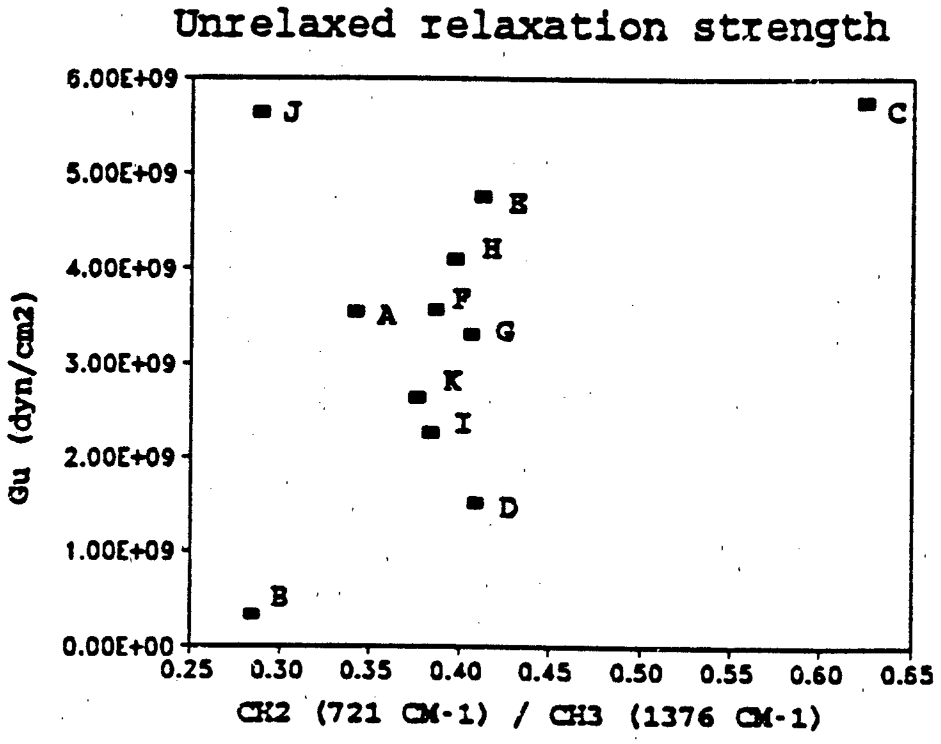

Figure A.7. Dependance of unrelaxed relaxation strength on chain length of asphalts.

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