Performance Modeling of Arabian Asphalt Using HP-GPC

I.M. Asi, H.I. Al-Abdul Wahhab, I.A. Al-Dubabi, and M.F. Ali

In this study, Arabian neat asphalt samples were collected from different asphalt producing refineries in the Gulf countries. Another set of polymer modified samples was also included in this study. In the polymer modification process, 5, 10, and 15% crumb rubber (CRT) and 3, 6, and 9% styrene-butadiene-styrene (SBS) were used. All asphalt samples were subjected to two aging processes to simulate heating, mixing, compaction, and in-service aging. The asphalt samples at the different aging stages were subjected to performance-based tests that were adapted and/or modified by the Strategic Highway Research Program (SHRP) team. High pressure gel permeation chromatography (HP-GPC) was used to chemically analyze the test samples by generating profiles of their molecular size distribution. Models were built to predict the performance-based properties from the produced HP-GPC profiles.

Keywords aging, asphalt, butadiene, HP-GPC, performance, permeation, polymers

1. Introduction

In the Gulf countries, asphalt pavement shows signs of high severity distress in the early stages of service. One of the main factors contributing to this distress is asphalt cement (AC). Asphalt cement is characterized by viscous and elastic properties. Two tests, penetration and viscosity, are used to classify asphalt cement and to test its suitability for use under certain loading and environmental conditions. The tests cannot be used to predict the performance of the asphalt. In 1992, the Strategic Highway Research Program (SHRP) developed a new set of tests that have the ability to predict asphalt performance because they rely on fundamental asphalt properties. Strategic Highway Research Program tests are time consuming and require expensive, complicated equipment and highly trained operators. Therefore, there is a need to find a simple, reliable, and fundamental test that can be used by asphalt manufacturers for process control and performance prediction.

High pressure gel permeation chromatography (HP-GPC) is one of the most advanced techniques used in characterizing the molecular distribution of liquid materials. It is available at a number of local institutions and oil refineries. It will be possible to use this device to predict asphalt performance if a set of models that relate HP-GPC profiles to performance properties can be developed. High pressure gel permeation chromatography has not been used as a standard test for the evaluation of asphalt cement, and no models have been generated to predict asphalt performance based on HP-GPC profiles.

Currently, there are four asphalt producing refineries in the Gulf countries: the Ras Tanura and Riyadh refineries in Saudi Arabia, the Al-Ahmadi refinery in Kuwait, and the BAPCO refinery in Bahrain. The asphalt produced by these refineries is referred to as "Arabian asphalt" and is included in this study.

In this research, the possibility of using HP-GPC chromatograms to predict asphalt performance behavior is evaluated. Mathematical models are generated to predict performance of asphalt cement based on molecular size. The goal in creating these models is to increase the understanding of asphalt behavior and the suitability of using a specific asphalt under prevailing loading and temperature conditions.

2. Objectives

The main goal of this research is to develop regression models that can be used to predict performance properties of Arabian asphalt from HP-GPC chromatograms. Models will be used to fingerprint asphalts suitable for each temperature range within the Gulf region. To achieve this goal, the following objectives were identified:

- To study performance related properties and HP-GPC chromatography of Arabian asphalts
- To study the effect of aging and polymer modification on the molecular size distribution of asphalt
- To recommend and modify a suitable procedure for the analysis of different chromatograms produced by HP-GPC

3. Collection of Asphalt Samples

Asphalt cement samples were collected from all asphalt producing refineries in the Gulf region. Those refineries were:

- Ras Tanura Refinery located in Eastern Saudi Arabia (RT)
- Riyadh Refinery located in Central Saudi Arabia (RY)
- Al-Ahmadi Refinery located in Kuwait (KW)
- BAPCO Refinery located in Bahrain (BH)
- Awazel Company located in Riyadh. (This company obtains asphalt cement from the Riyadh refinery [60/70 penetration* asphalt] and air blows it to obtain a harder asphalt [40/50 penetration asphalt].) (AZ)

Every month, a sample was collected from each refinery, totaling five samples per refinery, to achieve variability within sam-

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*Penetration is the consistency of an asphalt cement expressed as the distance in tenths of millimeters that a standard needle vertically penetrates a sample of the material at 25 °C, 100 g load, and 5 seconds time.

ples collected from the same refinery. In addition, one sample was collected from the Awazel Company. The total number of collected neat samples was 21.

Another set of samples was collected from a batch of polymer modified samples prepared for the "Adaptation of SHRP Performance Based Asphalt Specifications to the Gulf Countries" project (Ref 1). In the polymer modification process, one sample from each refinery was modified using 5, 10, and 15% crumb rubber (CRT) and 3, 6, and 9% styrene-butadiene-styrene (SBS). Details of mixing procedures of the polymers with the fresh asphalts can be found in Ref 1. The number of polymer modified samples was 24, making the total number of samples used in this research 45.

4. Experimental Program

Figure 1 shows work flow in this research. The collected asphalt samples were subjected to the required performance related tests suggested by SHRP in addition to fractionation by HP-GPC. Results were used to develop models to relate performance related properties to HP-GPC produced chromatograms.

4.1 *Performance Related Tests*

Recommended SHRP performance tests were performed on all asphalt samples to grade them according to the SHRP grading system and to determine the performance related properties of each sample. The following performance related tests were included.

4.1.1 Rotational Viscosity

A Brookfield viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA) was used to measure the rotational viscosity of the different asphalt samples. The ASTM D 4402 method, "Viscosity Determination of Unfilled Asphalts Using the Brookfield Thermosel Apparatus," was followed.

4.1.2 Aging of Asphalt Samples

Two stages of aging are applied to the asphalt samples. The first aging procedure simulates short-term aging of the asphalt that occurs due to heating, mixing, and compaction. This aging process was performed using Cox & Sons rolling thin film oven (RTFO; James Cox & Sons Inc., Colfox, CA) to obtain the required RTFO residue. The AASHTO T240 and ASTM D 2872 standard test procedures were used. The other aging process was performed using a pressure aging vessel (PAV) to simulate eight to ten years of in-service. The PAV was used according to the AASHTO PP1 "Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel" test procedure. All pressure aging was performed on samples previously aged by RTFO. These aging processes were required to prepare the asphalt samples for further testing.

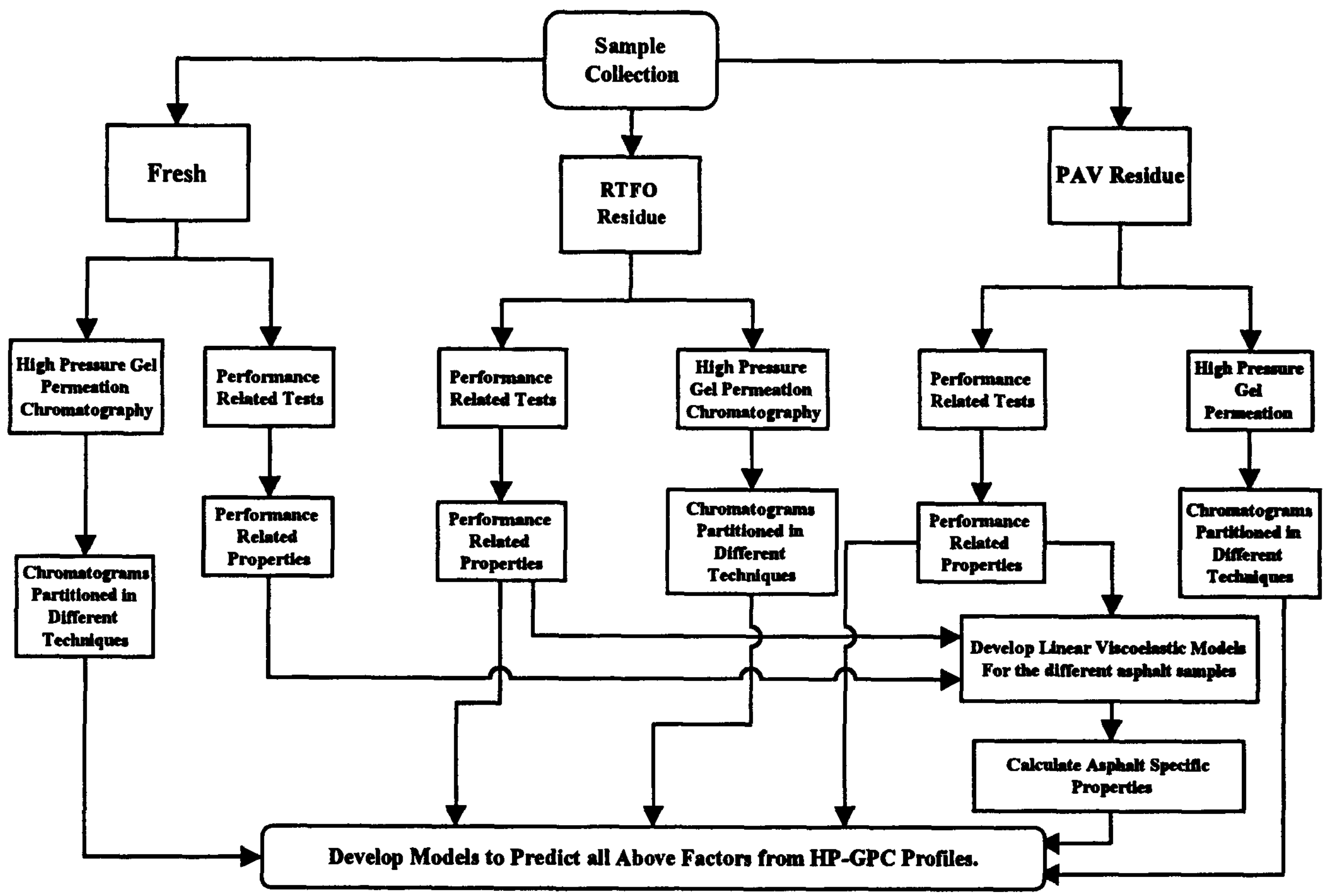

Fig. 1 Flow chart of the planned work

4.1.3 Dynamic Shear Rheometer Testing

The Bohlin dynamic shear rheometer (DSR; Bohlin Instruments, Granbury, NJ) was used to determine the complex modulus (G^*) and the phase angle (δ) for all test samples. The AASHTO TP5 standard method of testing for "Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer" was followed. The test apparatus consisted of a DSR and a temperature controller, and a computer was used to control the rheometer and acquire data.

4.1.4 Bending Beam Rheometer Testing

The Fisher bending beam rheometer (BBR; Canon Instruments Co., State College, PA) was used to measure the creep stiffness (S) and logarithmic creep rate (m-value) of all test samples. The BBR test can be performed on PAV residue or fresh samples. For SHRP grading, it must be performed on PAV residue. In this research, the test procedure, AASHTO TP1 "Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer," was followed.

4.2 *HP-GPC Testing*

High pressure gel permeation chromatography is widely used in the analysis of petroleum residues and asphalts. Although the interpretation of the HP-GPC output is not as straightforward with asphalts as with polymers, the method allows relative determination of molecular size and molecular weight.

The Waters high pressure liquid chromatography (HPLC) system 840 (Waters Chromatography, Milford, MA) was used in this research with a model 501 pump, a 712 WISP auto injector, and a R-401 refractometer as a detector. To control the HP-GPC system and collect, analyze, save, and retrieve the collected data for future use, Millenium 2010 Chromatography Manager software (Waters Chromatography, Milford, MA) was attached to the system. Four micro styra-gel columns were connected in the following order according to porosity size: 10,000, 1000, 500, and 100 Å. The columns were attached to the differential refractive index (RI) detector. This detector was used to detect differences in the refractive index between the carrier solution and the sample stream. The greater the difference, the greater the response. Tetrahydrofuran (THF) (HPLC grade) was used to dilute the asphalt samples and was used as the mobile phase. The experimental procedure followed in this research was based on published methods (Ref 2-4) with the introduction of needed modifications.

4.3 *Fractionating Procedure of the HP-GPC Chromatograms*

The initial output of the computer after running the samples through the porous columns was a graphical presentation of the change in voltage (in mV) sensed by the differential refractometer due to the difference of the refractive index between the carrier solution and the sample stream versus time of elution in minutes. Figure 2 shows the superimposed produced chromatograms for BH1, BH1-RTFO, and BH1-PAV samples. This figure shows the ability of the system to detect differences between asphalts exposed to different aging processes.

After studying the general shapes of the produced profiles, it was decided to restrict the analysis of the data for the elution period to 22 to 38 minutes. The Millenium Chromatography Manager was reused to slice the area under the chromatograms into one thousand slices. The program gave the timing for each slice and the area under each slice. Response was an indicator of the concentration of asphalt molecules in the solution. The slices were grouped into different fractions. The HP-GPC chromatograms were fractured to quantify them. Different fractionating procedures were used in this research to discover the most appropriate procedure to explain the shape of the produced profiles. Eight methods of fractionating the produced chromatograms were used:

- Using three equal time slices
- Using three equal average area slices
- Fractionating into three slices of 25, 50, and 25% of total time
- Fractionating into three slices of 25, 50, and 25% of total area
- Fractionating into eight equal time slices
- Slicing into eight equal time fractions
- Slicing into twelve equal time fractions
- Slicing into twelve equal area fractions

In Fig. 2, two fractionating procedures are shown: fractionating into eight equal time fractions and eight equal average areas. The produced fractions are numbered sequentially from X1 to X8 from left (larger size) to right (smaller size). The area under each slice is calculated and used in the model building.

Two other factors that were used in this research to better quantify the shape of the produced profiles were the standard

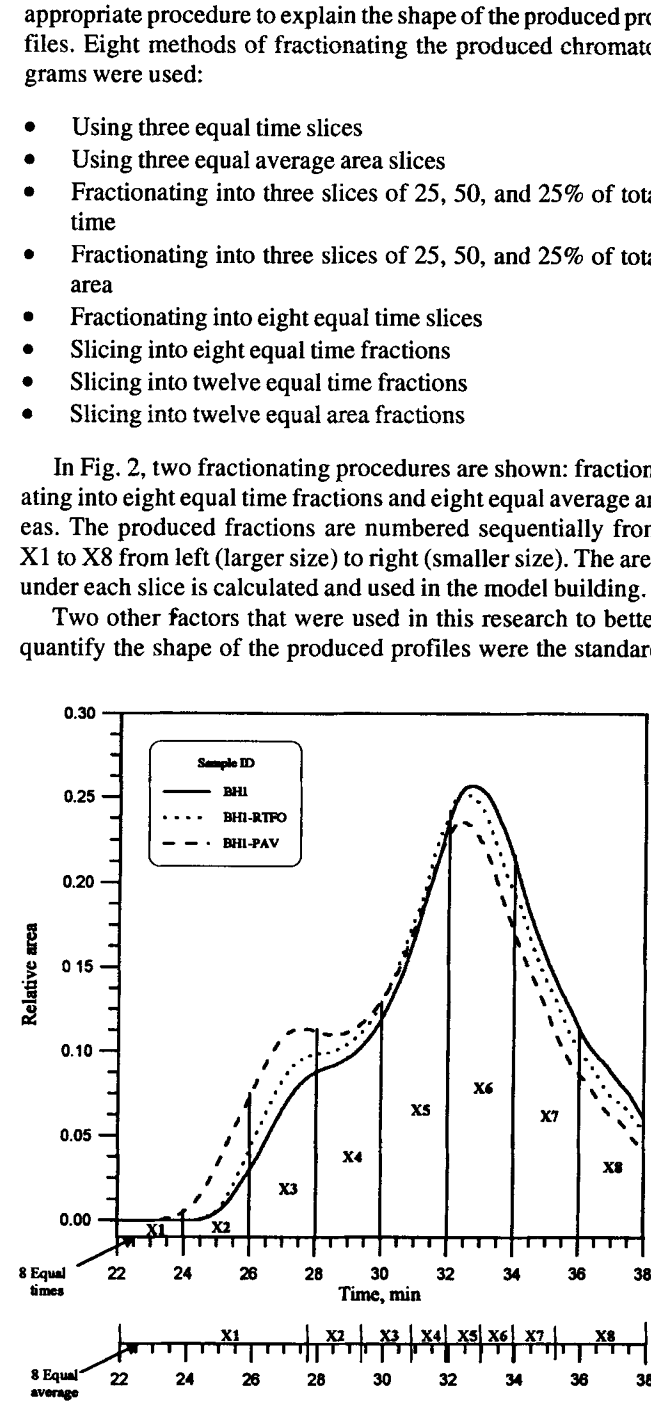

Fig. 2 HP-GPC chromatogram for the BH1 sample after processing and slicing into 8 slices

deviation and the skew of the different fractions. The standard deviation is a measure of how widely values are dispersed from the average value (the mean), and skew characterizes the degree of asymmetry of a distribution around its mean. Positive skew indicates a distribution with an asymmetric tail extending toward more positive values. Negative skew indicates a distribution with an asymmetric tail extending toward more negative values. These two factors indicate the general shape of the produced profiles. They were used in the correlation studies between the HP-GPC and other suggested properties.

4.4 *Construction of the Master Curves*

Because one of the objectives of the study is to correlate performance-based properties with molecular size distribution of the asphalt samples, it was determined that the best way to achieve this was by finding asphalt specific properties (independent of temperature and rate of loading) and correlating them with the molecular size distribution. Those properties are obtained through the use of the linear viscoelastic model (LVE) of each asphalt. The LVE is a mathematical model that describes the asphalt and the linear viscoelastic response of asphalt cements at the different test temperatures and different frequencies (Ref 4). The behavior of any asphalt at any temperature can be predicted using only three parameters: the defining temperature T_d, the crossover frequency ω_0 (or crossover time t_0), and the rheological index R. The defining temperature uniquely characterizes the shift factors as a function of temperature. The rheological index is a representation of the rheological behavior of the asphalt and is directly proportional to the elastic behavior of the asphalt at intermediate temperatures. The crossover frequency indicates the location of the master curve at the selected reference temperature and is an indication of the hardness of the asphalt (Ref 5). These parameters are asphalt specific and can be used in analyzing the rheological properties of each asphalt, in comparing asphalts, and in developing chemical-physical property relationships. The LVE models were generated, and the asphalt specific parameters were calculated for all samples. Figure 3 shows a plot of the master curves for RY1 samples at all test temperatures and at the defining temperature.

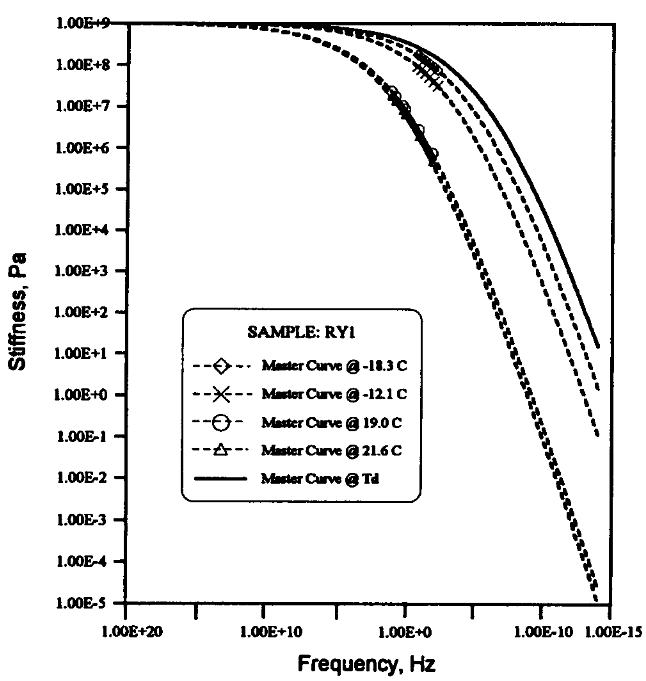

Fig. 3 Master curves of the RY1 sample at the test temperatures and at the defining temperature

5. Results and Discussion

Table 1 shows the grading of the asphalt samples. For all nonmodified samples, the upper grading limit was 64 °C. Conversely, for modified samples, the upper grading limit ranged between 70 and 80 °C. The lowest grading limit for all samples

Table 1 SHRP grading of the collected samples

Sample	Grading
RT1	PG 64-22
RT2	PG 64-22
RT3	PG 64-22
RT4	PG 64-28
RT5	PG 64-28
BH1	PG 64-28
BH2	PG 64-22
BH3	PG 64-22
BH4	PG 64-22
BH5	PG 64-22
RY1	PG 64-22
RY2	PG 64-22
RY3	PG 64-22
RY4	PG 64-22
RY5	PG 64-22
KW1	PG 64-22
KW2	PG 64-22
KW3	PG 64-22
KW4	PG 64-22
KW5	PG 64-22
AZ1	PG 70-22
RT-CRT-5%	PG 70-28
RT-CRT-10%	PG 76-22
RT-CRT-15%	PG 82-28(a)
RT-SBS-3%	PG 76-22
RT-SBS-6%	PG 82-22(a)
RT-SBS-9%	PG 82-22(a)
RY-CRT-5%	PG 70-22
RY-CRT-10%	PG 76-22
RY-CRT-15%	PG 82-28(a)
RY-SBS-3%	PG 82-22
RY-SBS-6%	PG 82-22(a)
RY-SBS-9%	PG 82-16(a)
BH-CRT-5%	PG 70-22
BH-CRT-10%	PG 70-22
BH-CRT-15%	PG 82-28(a)
BH-SBS-3%	PG 76-22
BH-SBS-6%	PG 82-16(a)
BH-SBS-9%	PG 82-16(a)
KW-CRT-5%	PG 82-16
KW-CRT-10%	PG 82-22(a)
KW-CRT-15%	PG 82-22(a)
KW-SBS-3%	PG 76-22
KW-SBS-6%	PG 82-22(a)
KW-SBS-9%	PG 82-16(a)

(a) Rotational viscosity is higher than 3000 centi-Pascal-second.

ranged between −16 and −28 °C. The addition of a polymer improved the upper limit of all samples. However, there was no specific effect of the polymer on the lower grading temperature. Some of the polymer modified samples failed the set criteria for maximum allowable rotational viscosity but were included in the grading with an asterisk. This was done because SHRP grading allows this if it is safe to pump and mix the binder at a higher temperature than normally used.

Performance grades for all neat samples were either PG 64-22 or PG 64-28. This implies that these asphalts are suitable for an upper pavement temperature limit of 64 °C and a lower air temperature of −22 or −28 °C. In the Gulf region, pavement temperatures reach higher temperatures than the upper grading temperature of local asphalts (Ref 1), which ensures the need for polymer modification. As shown in Table 1, polymer modification raised the upper grading limit of local asphalts to 80 °C, which is even higher than expected pavement temperatures in the region.

The HP-GPC analysis was performed on all samples at the different stages of aging. This technique was capable of giving profiles for the molecular size distribution of all tested samples. To check the profiles for the samples from each source (RT, RY, BH, KW) for unique shapes distinguishing them from asphalts belonging to other sources, neat samples from each source were drawn on the same graph (e.g., Fig. 4 and 5 show the produced HP-GPC profiles for RT and KW samples, respectively). Figure 6 includes profiles of the first sample collected from each source. Samples from each source exhibit some shape characteristics that differentiate them from samples from other sources. This shows the ability of the system to differentiate between samples produced from different resources. Figure 7 shows the effect of polymer quantity and polymer type on the produced HP-GPC profiles. In Fig. 7, the skew factor for the produced HP-GPC chromatograms of the polymer modified samples were drawn. There is an increase in the skew value with the increase in the polymer percentage. The increased skew indicates that there is an abundance of cases with lower scores, that is, there is a shift in the profile to the left because there is an increase in the larger size molecules. Also, Fig. 7 shows that SBS is more effective than CRT in shifting the molecular size distribution to the left and increasing the relative amounts of the large molecular size.

In general, the following are true for the produced HP-GPC chromatograms:

- HP-GPC analysis can detect the effect of aging, polymer modification, asphalt source, and asphalt production on the molecular size distribution.
- There is an increase in the amount of large molecular size fraction as a result of oxidation.
- The addition of polymer increased the amount of larger molecule size (LMS) on account of smaller molecule size (SMS).
- Styrene-butadiene-styrene (SBS) has a higher effect in increasing the amount of LMS.
- Transformation of the molecular size seems to be the cause of the change in physical properties that occurs due to aging.
- The increase in the amount of LMS leads to a decrease in the penetration value and an increase in the viscosity of the asphalt cement (AC).

6. Modeling the Properties of Asphalt Using Produced HP-GPC Chromatograms

A total of 45 samples were used to generate the correlation models (21 fresh samples and 24 polymer modified samples). Of those 45 samples, 37 were used for generating the different models, and the other 8 samples were chosen randomly for model validation.

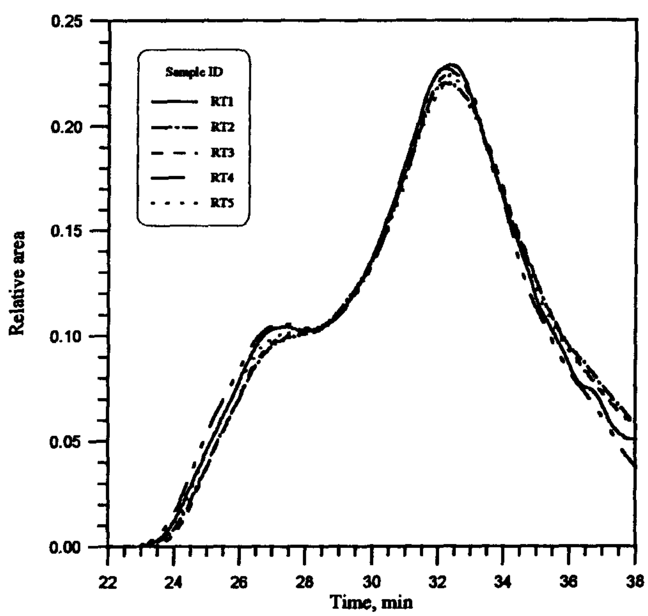

Fig. 4 HP-GPC chromatograms for RT samples

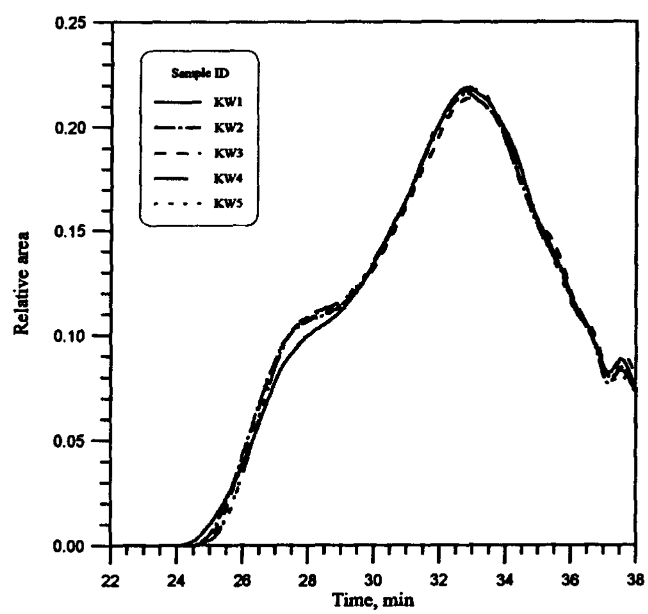

Fig. 5 HP-GPC chromatograms for KW samples

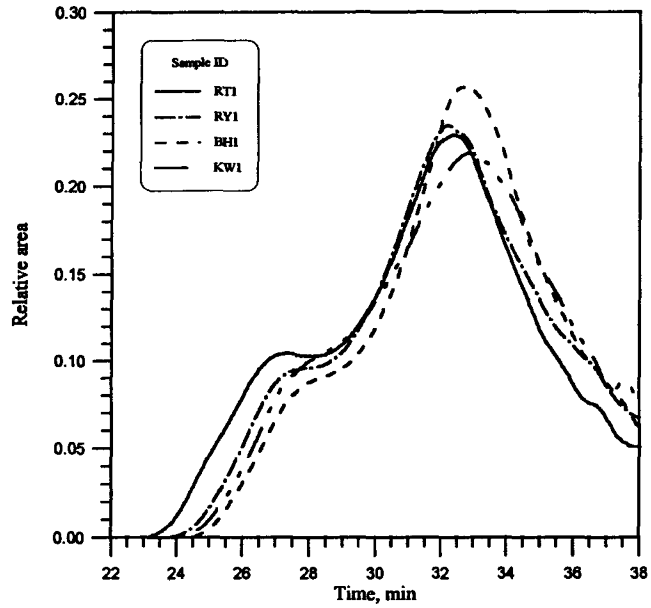

Fig. 6 HP-GPC chromatograms for the first sample collected from each asphalt source

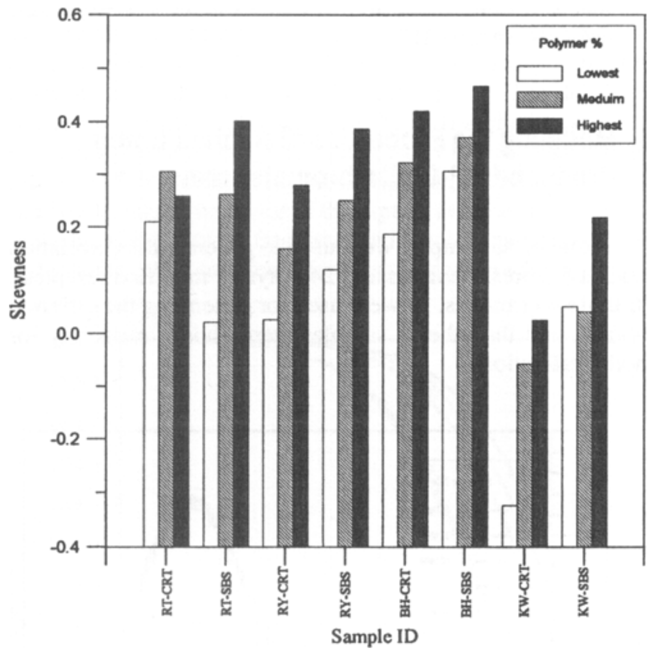

Fig. 7 Effect of polymer percentage on the skew of the produced HP-GPC chromatograms

In the prediction models, the dependent variable was any of the performance-based properties of the AC. Table 2 lists the properties used. The independent variables were those fractions into which the HP-GPC profiles were fractionated, in addition to the skew factor and the standard deviation of those fractions, taking each fractionating procedure separately. Because the total number of variables in each model is as high as 14 and because it is difficult to predict exactly which fraction contributes more to any of the properties, especially with the

Table 2 Properties and indices used in this study

Symbol used	Property
Grading	
Lower	Lower grading temperature, °C
Upper	Upper grading temperature, °C
LVE parameters	
Gg	Glassy moduli, GPa
R	Rheological index
w_0	Crossover frequency at Td, Hz
η_0	Steady-state viscosity at Td, GPa-s
Design parameters	
$G^*/\sin\delta$	$G^*/\sin\delta$ at 64 °C, MPa
$G^* \times \sin\delta$	$G^* \times \sin\delta$ at 25 °C, MPa
S (60)	Creep stiffness at 60 Hz at 0 °C, MPa
m (60)	Creep rate at 60 Hz at 0 °C

high number of fractions, stepwise regression was used. Stepwise forward-selection regression was used to correlate each factor with the different fractions of each fractionating process. The purpose of the stepwise regression was to help select a smaller subset, which would adequately explain the response, from the total number of variables in each procedure. The criterion for including any factor in the regression model was set to be 1.0; that is, the variable would be included in the model if it added to the significance level of the F-ratio, a value of 1.0.

To determine which fractionating procedure best explains the prediction parameters, stepwise forward-selection regression was used to relate the dependent variables to the fractions of each fractionating procedure. The coefficient of determination (R^2) was used to judge the adequacy of the generated regression models because it elicits variability in the data explained or accounted for by the regression model. For the purpose of comparison, no transformation of the data was performed at this stage of study. Table 3 lists the values of R^2 for the different models using the different fractionating procedures. Also included are the average values of R^2 and standard deviations. Table 3 shows that there is an increase in the average value of R^2 with the increase in the number of fractions. A large increase in the average value of R^2 is obtained for 8 and 12 for the 3 fractions. Equal time fractions gave better results than equal areas. The average R^2 value increased from 0.15, when using 3 equal time fractions, to 0.52 when using 12 equal time fractions, indicating that the increase in the number of fractions will add to the degree of explanation of the model. Table 3 shows that the rate of increase in R^2 with the increase in the number of fractions is high, but this rate decreased gradually with the increase in the number of fractions. Therefore, 12 fractions of equal times was used in the modeling work for the completion of this study. Increasing the number of fractions to more than 12 would not be feasible because a large number of samples is needed for model development, and from a practical point of view, the models would be too complicated.

The asphalt properties in general are known to be affected by the aging of the AC. It is believed that using the HP-GPC produced profiles for the RTFO residue in the prediction models will give better determination coefficients. The produced

Table 3 R-square of the different models using stepwise regression

Property	HP-GPC fractioning procedure							
	3 equal times	3 equal areas	3 times (25, 50, 25%)	3 areas (25, 50, 25%)	8 equal times	8 equal areas	12 equal times	12 equal areas
Lower grading temperature, °C	0.0852	0.2368	0.1087	0.1555	0.5364	0.3588	0.6497	0.4769
Upper grading temperature, °C	0.4420	0.4281	0.4842	0.4185	0.7111	0.6947	0.7155	0.6391
Gg, GPa	0.0673	0.2763	0.0000	0.3570	0.8235	0.1310	0.9784	0.2270
R	0.2705	0.2898	0.3000	0.3569	0.6708	0.2548	0.6923	0.3722
ω_0 at Td, Hz	0.2275	0.1571	0.1131	0.1392	0.1715	0.1680	0.2570	0.1617
η_0 at Td, GPa-s	0.0000	0.1217	0.0000	0.2152	0.2694	0.3459	0.3549	0.2074
$G^*/\sin\delta$ at 64 °C, MPa	0.0000	0.0522	0.0000	0.0389	0.0336	0.0494	0.3775	0.1127
$G^* \times \sin\delta$ at 25 °C, MPa	0.1214	0.0972	0.1403	0.1058	0.1382	0.1176	0.3207	0.1533
S(60) at 0 °C, MPa	0.1506	0.1072	0.1737	0.1210	0.2735	0.1737	0.3554	0.3190
m(60) at 0 °C	0.1692	0.1344	0.1243	0.1176	0.4341	0.5372	0.5037	0.7281
Average	0.1534	0.1901	0.1444	0.2026	0.4062	0.2831	0.5205	0.3397
Standard deviation	0.1345	0.1153	0.1512	0.1294	0.2702	0.2041	0.2306	0.2132

Table 4 Generated models for different parameters

Property	Suggested model	R^2	Significant level
Lower grading temperature, °C	(Lower) = 1/(− 0.191 − 0.017 × 1 + 0.005 × 4 + 0.014 × 6 − 0.004 × 8 + 0.012 × 10 − 0.018 STDEV + 0.090 skew)	0.6926	0.0000
Upper grading temperature, °C	Upper = (23.419 − 0.309 × 3 − 0.595 × 5 − 0.216 × 9 − 0.350 × 12 − 0.679 STDEV − 0.741 skew) ^2	0.8802	0.0000
Gg, GPa	Gg = 126.506 − 1.330 × 3 − 4.113 × 5 − 6.817 × 6 + 2.719 × 7 − 1.125 × 8 − 1.954 × 9 − 22.904 skew	0.9427	0.0000
R	R = EXP (5.698 − 0.339 × 5 − 0.057 × 9 − 0.163 × 12 − 0.793 skew)	0.7156	0.0000
ω_0 at Td, Hz	ω_0 = 1/(1.335E08 − 4.047E07 × 2 + 3.531E07 × 3 − 1.404E07 × 4 − 1.373E07 × 8 + 2.301E07 STDEV + 7.085E07 skew)	0.5432	0.0007
η_0 at Td, GPa-s	η_0 = 5.044E07 − 3.615E07 × 2 + 3.111E07 × 3 − 1.533E07 × 4 + 1.599E07 skew	0.5001	0.0003
$G^*/\sin\delta$ at 64 °C, MPa	$G^*/\sin\delta$ = EXP (51.210 − 1.615 × 2 + 2.434 × 3 − 6.698 × 4 + 9.953 × 5 − 6.422 × 6 − 1.008 × 9 − 2.604 × 11)	0.6367	0.0001
$G^* \times \sin\delta$ at 25 °C, MPa	$G^* \times \sin\delta$ = EXP (− 176.868 + 2.994 × 2 + 1.460 × 3 + 9.338 × 5 + 2.254 × 8 + 3.076 × 10 + 3.010 × 12 + 15.321 skew)	0.6367	0.0001
S(60) at 0 °C, MPa	S = 1/(− 7.435E08 + 2.131E07 × 1 + 3.354E07 × 2 + 3.210E07 × 8 + 1.374E07 × 9 − 8.334E06 × 10 + 1.191E07 × 12 − 2.244E08 skew)	0.7788	0.0000
m(60) at 0 °C	m = 1/(4.785 − 0.155 × 2 − 0.100 × 7 − 0.091 × 8 + 0.263 × 9 − 0.319 × 10)	0.5962	0.0000

EXP (x) = e^x and x^2 = x^2

Table 5 Prediction of the generated models for the performance grades of the validation samples

Sample	Performance grade, measured	Upper temperature (predicted), °C	Lower temperature (predicted), °C	Performance grade (predicted)
RT3	PG 64-22	66.24	−21.26	PG 64-22
RY1	PG 64-22	62.46	−19.65	PG 64-22
BH3	PG 64-22	63.84	−19.94	PG 64-22
KW5	PG 64-22	65.19	−20.80	PG 64-22
RT-SBS-3%	PG 76-22	80.83	−17.08	PG 80-16
RY-CRT-10%	PG 76-22	73.94	−21.31	PG 76-22
BH-CRT-15%	PG 80-28	79.51	−26.81	PG 80-28
KW-SBS-3%	PG 76-22	73.62	−20.52	PG 76-22

profiles for the RTFO residue of the different asphalt samples were partitioned into 12 fractions. Stepwise regression was used to produce models for all prediction parameters. The average R^2 value became 0.58, which clearly shows an increase in the average value of R^2 when using RTFO chromatograms. Twelve fractions of equal time for the RTFO produced chromatograms have the higher average R^2 value and are used in model generation.

To check the linearity of the relationship between the dependent variables (DV) and the independent variables (IV), graphs were drawn to show the relationship between each DV and the IVs. The shapes of the graphs were studied to check if the relationship was linear or if some sort of mathematical transformation for either the DV or the IV was needed. Required transformations were made, and the models were rebuilt. Table 4 shows the transformed models with their R^2 and significance levels. In these models, XI represents the fraction number, skew represents the measured skew factor between the different fractions, and STDEV represents the standard deviation of the twelve fractions. Determination of the coefficient is represented by R^2, which gives the amount of the variability in the DV explained by the suggested model. All R^2 values for the models were found to be over 0.50. All suggested models have a level greater than 95%, which implies that at 95%, at least one of the independent variables in each of the generated models contributes significantly to the regression.

To check the ability of the model to predict the lower grade of the verification samples, Table 5 shows the prediction of the generated models for the performance grades of the validation data. Of the eight validation samples, the upper and lower temperature grading models were used to predict their grades. Seven samples were graded correctly, while the eighth sample was incorrect. This is an acceptable level of error because the R^2 for the upper and lower grading temperature models is 0.88 and 0.69.

7. Conclusions

This study achieved the set objectives and arrived at the following conclusions:

- Mathematical LVE models that can be used to evaluate asphalt performance over a wide range of temperatures, loading times, and stress or strains were developed for locally produced modified and neat asphalts.
- The molecular size distribution of the asphalts is affected by aging, polymer modification, and asphalt source. Aging and polymer modification increase the amount of larger molecular size fractions because of the smaller molecular size fraction.
- The best observed method to quantify the produced HP-GPC chromatograms is to slice them into 12 fractions with equal elution times.
- Styrene-butadiene-styrene was more effective than CRT in increasing the relative amounts of larger molecular size fractions.
- Two additional factors proved to be helpful in characterizing the shape of the produced chromatograms. They are skew and standard deviation of the different sliced fractions.
- Using HP-GPC chromatograms of RTFO or thin film oven (TFO) residue gives better prediction results than fresh samples.
- Prediction models were generated for the different performance-based properties from HP-GPC chromatograms.

Acknowledgments

The authors would like to acknowledge King Fahd University of Petroleum & Minerals (KFUPM) and King Abdulaziz City for Science and Technology (KACST) for funding the project entitled "Adaptation of SHRP Performance Based Specifications for Gulf Countries." This paper is part of that project.

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