HP-GPC CHARACTERIZATION OF ASPHALT AND MODIFIED ASPHALTS FROM GULF COUNTRIES AND THEIR RELATION TO PERFORMANCE BASED PROPERTIES

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INTRODUCTION

Asphalt producing refineries in the Gulf countries include Ras Tanura and Riyadh (Saudi Arabia), Al-Ahmadi (Kuwait), and BAPCO (Bahrain). Riyadh and Ras Tanura refineries are located in the central and eastern Saudi Arabia respectively. Arabian light crude oil is used to produce 2000 to 3000 tons of asphalt per day using vacuum distillation, air blowing and grade blending techniques to produce 60/70 penetration grade asphalts in each of these two Saudi refineries. All of the asphalt cement used in Saudi Arabia, Qatar and parts of the United Arab Emirates is supplied by Riyadh and Ras Tanura refineries.

Al-Ahmadi refinery supplies all of the asphalt cement needed for construction in the state of Kuwait. Ratwi-Burgan crude oil mix is used to produce 750 to 1000 tons of asphalt per day using vacuum distillation and air blowing processes.

BAPCO refinery, Bahrain, utilizes crude oils produced from Saudi oil fields and supplies asphalt cement needed for construction in Bahrain, Oman and parts of United Arab Emirates.

The roadway network in Gulf countries has developed more rapidly than in many industrialized countries. The entire roadway network is built using flexible pavements due to the availability of relatively low cost asphalt binders. The asphalt binder plays a significant role in pavement ability to withstand thermal and fatigue cracking and contribute to permanent deformation behavior. Fatani et al [1] in a study about permanent deformation in Saudi Arabia have concluded that the asphalt cement is responsible for a major part of rutting in the region, and that extreme weather conditions of the Gulf countries has promoted an inferior performance of asphalt concrete mixes in the field.

Asphalt binders are thermo-visco-elastic materials where temperature and rate of load application has a great influence on their behavior. Asphalt consistency and hence ability to sustain and hold their fundamental cementing mechanism changes depending on temperature. The pure asphalt lack the proper balance of viscous fluid-elastic sponge properties which usually occur due to an effective elastic network created by molecular association. In recent years various studies have shown that polymer modification can be successful in forming this viscous fluid-elastic sponge balance by creating molecular entanglement in an asphalt.

This study was initiated to evaluate different locally available polymer materials in order to identify potential polymers to modify asphalts to satisfy the performance requirements in the Gulf countries' environmental conditions. The storage stability of the asphalt-polymer blends and the life cycle cost analysis of the polymer modification were also studied.

EXPERIMENTAL

1. Temperature data collection and temperature zoning: Metrology and Environmental Protection Agencies, Directorate of Climatology and other similar agencies in the Gulf countries were approached to provide the research team with the available historical annual environmental data covering the Gulf countries (GC). These data were analyzed and used to build temperature data base and to develop suitable temperature zoning for the GC.

2. Asphalt samples collection: Asphalt binder samples were collected from all asphalt cement producing refineries in the Gulf which include Ras Tanura and Riyadh (Saudi Arabia), Al-Ahmadi (Kuwait), and BAPCO (Bahrain) and an additional sample was collected from Awazel private company which modifies asphalt produced by Riyadh refinery.

3. Asphalt testing: Collected asphalt samples were subjected to comprehensive testing to determine their physical and chemical properties. Testing included:

a. Consistency testing; viscosity at 25°C (ASTM D 3570), 60°C (ASTM T-202-80) and 135°C (AASHTO T-201-80), penetration at 25°C and 4°C (AASHTO T-49-80), softening point (AASHTO T-53-81) and ductility (AASHTO T-51-81). Testing was carried out on fresh and rolling thin film oven (RTFO) residue (AASHTO T-240-78).

b. Performance based testing which was performed on original binder, RTFO residue and pressure aging vessel (PAV) residue [2]. Tests included flash point, rotational viscosity, dynamic shear, mass loss after RTFO, flexural creep stiffness and direct tension failure strain [2].

c. Chemistry, chemical composition of collected samples were determined using Corbett's method, ion exchange chromatography and high pressure gel permeation chromatography (HP-GPC).
The HP-GPC procedure for this study utilized four µ-styragel columns connected in the following order according to size: 10,000, 1000, 500 and 100 Å. Two kinds of detectors, a differential refractometer and a UV absorbance detector (230 nm and 340 nm) were used. HPLC grade tetrahydrofuran (THF) was used as a solvent mobile phase at ambient temperature (24°C) at a flow rate of 1.0 ml/min. the data were accumulated by a millennium 2010 chromatography manager.

4. Asphalt Modification: Asphalt cement which has a performance grade that does not satisfy the binder specification as determined by temperature zoning was modified to improve its quality. Modified binders were subjected to the same set of tests as virgin asphalts.

RESULTS AND DISCUSSION

Asphalt Testing: The complete test results for the collected asphalt samples, temperature data and contour map were published in Al-Abdul Wahhab et al [3].

Results indicate that asphalt cement produced in the Gulf satisfies the low temperature requirement but can only satisfy one zone of 64°C average seven day consecutive maximum temperature. Awazel air blown asphalt met the requirement of PG 70-10 while PG 58-10 and PG 76-10 zones have not been met. This indicates the necessity of modifying locally produced asphalts to meet the performance requirements of these temperature zones.

ASPHALT MODIFICATION

The asphalt modification work was carried out in two phases. The first phase focused on identifying potential polymers while the second focused on the optimization of modification process for the following selected polymers:

LLDPEX - Linear low density polyethylene grade 1182
PP500C - Polypropylene grade 500V
SBS - Styrene - butadiene - styrene

A fourth polymer, crumb rubber from truck tires (CRT) was also included for this study. The polymer modified samples were subjected to physical tests.
Results showed that addition of the polymer material significantly improves the physical and rheological properties of Arab asphalt binders for all sources and all polymer types.

HP-GPC Analysis

A typical HP-GPC profile is shown in Fig. 1. The variable on the x-axis is the time required of a particular size to emerge from the system. The reading on the y-axis is the detector response, which is an indicator of the concentration of asphalt molecules in solution. In order to distinguish HP-GPC profiles, the area under the curve is divided into different sections. Most frequently this is divided into three sections and the area under each section in determined. These three areas are referred to as large-molecular size (LMS), medium-molecular size (MMS), and small-molecular size (SMS) material. However, other researchers felt that these three parameters could not adequately model the subtle differences between the HP-GPC profiles of the asphalts used. Accordingly, for this study a procedure was used in which the area under the curve was divided into eight sections (see Fig. 1). This number was selected as the optimum needed to provide an accurate quantitative model of the HP-GPC profiles.

The cut-off points were selected to have equal elution times. The eight sections are numbered from left to right. Consequently, apparent molecular size decreases progressively from Section 1 to Section 8.

Fig. 1 also compares GPC profiles for fresh, RTFO and PAV aged asphalts. There are clear differences in each of the curves, with the PAV aged and RTFO aged samples showing significant growth in the large-molecular size (LMS) region (material eluted between 24 and 30 minutes) for this sample. GPC profile Fig. 1 also shows the growth in LMS is accompanied by a gradual decrease in MMS and SMS regions. Profiles of parent asphalts, polymer modified asphalts, and RTFO/PAV asphalts are shown in Figs. 2, 3 and 4.

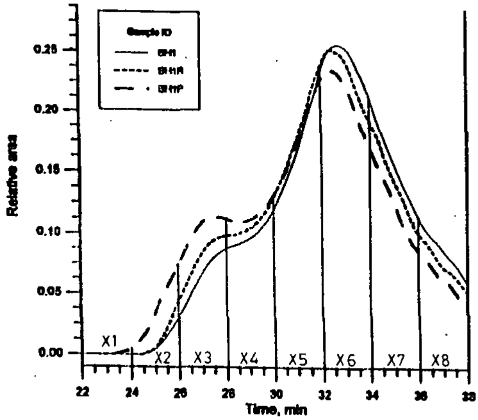

Fig. 1: HP-GPC profiles for original and oxidized asphalts

From the HP-GPC analysis it can be seen that all of the polymer modified asphalts have a larger percentage of fractions # 1, 2, 3 and 4 and a smaller percentage of fractions 5 and 6 than the parent AC-20. It is also apparent from the GPC profile that the fractions # 1, 2 and 3 have considerably increased for RTFO and PAV aged samples (Fig. 4) than modified non-aged asphalt.

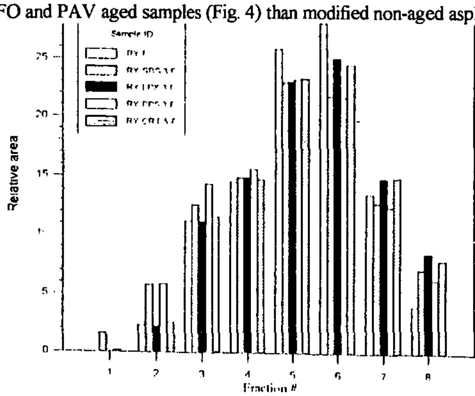

Fig. 2: HP-GPC partitions into Eights of parent AC-20 and polymer modified asphalts

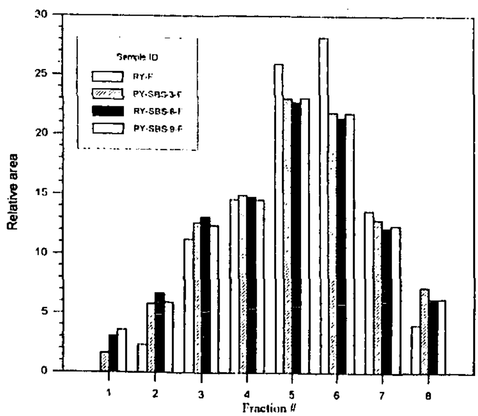

Fig. 3: HP-GPC partitioned into Eights of parent AC-20 and SBS-modified asphalts

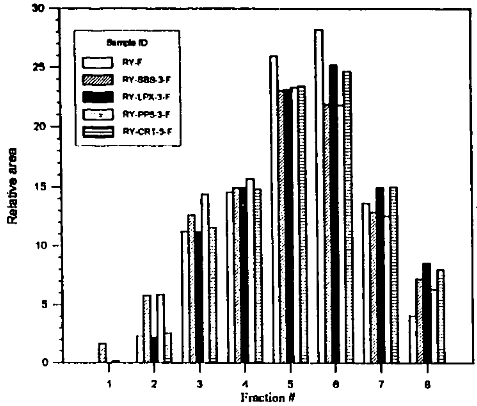

Fig. 4: HP-GPC partitioned into Eights of parent AC-20 and SBS-modified and their RTFO and PAV aged asphalts

Correlation Studies of Asphalt Composition with Its Performance-Related Characteristics :

This sub-task aims at finding the mathematical relation - if it exists - between the physical properties of the asphalt and its chemical composition. The physical properties which are included in this sub-task are shown in Table 1. The chemical composition is represented by the eight fractions (X_1 to X_8) into which the HP-GPC chromatograms were divided. X_1 was dropped from the analysis to get rid of interdependency between the eight fractions of the chromatograms, i.e. if X_1 is kept in the analysis, the sum of X's is always 100.

Table 1: Included physical properties

Used Symbol	Property
SG	Specific Gravity
PEN25	Penetration at 25°C
RPEN25	Retained Penetration at 25°C
PEN4	Penetration at 4°C
RPEN 4	Retained Penetration at 4°
SP	Softening Point
FP	Flash Point
DUC	Ductility
VIS25	Sliding Plate Viscosity at 25°C
VISR25	Viscosity Ratio at 25°C
VIS60	Absolute Viscosity at 60°C
VISR60	Viscosity Ratio at 60°C
RVIS135	Rotational Viscosity at 135°C
VIS135	Kinematic Viscosity at 135°C
VISR135	Viscosity Ratio at 135°C
PI	Penetration Index
PTS	Penetration Temperature Susceptibility
PR	Penetration Ratio
PVN	Penetration Viscosity Number
PVNI	Penetration Viscosity Number for VTS calculation
VTS	Viscosity Temperature Susceptibility
ω_o	Cross Over Frequency
R	Rheological Index
T_d	Defining Temperature
G*	Complex Dynamic Modulus, KPa
S	Flexural Creep Stiffness, MPa
m	Flexural Creep Slope

The purpose of the analysis is to help select from the 7 candidate variables X_2, X_3, ..., X_8 a smaller subset that will adequately explain the response. A number of variable selection procedures are available in the statistical literature. The most commonly used ones are the search over all possible subsets, the forward selection procedure and the stepwise selection procedure. The corresponding SAS PROC RSQUARE, SAS PROC FORWARD and SAS PROC STEPWISE were used and their results are noted. It is generally accepted that all stepwise procedure is vastly superior to the others and thus it is the one relied upon in this analysis.

Table 2 presents models for the different variables, together with their R^2 value and P-value for fresh and polymer modified samples.

Table 2: Regression analysis for fresh samples

Variable	Modification	Model	R^2	P-value
SG	No	$1.09 - 0.003X_3 - 0.002X_6$	0.53	0.0011
PEN25	No	$74.04 + 1.02X_3 - 1.67X_6$ P-value for testing significance of X_3 is 0.12	0.32	0.0297
RPEN25	No	$1.99 + 0.04X_3 - 0.08X_6 - 0.01X_7$ P-value for testing significance of X_7 is 0.10	0.85	0.0001
PEN4	No	$44.1 + 1.43X_3 - 0.9X_6$	0.71	0.0001
RPEN4	No	$0.14 + 0.03X_3 + 0.02X_6$	0.32	0.0316
SP	No	$-44.23 + 2.95X_3 + 0.47X_4 + 1.96X_6 + 1.55X_8$ P-value for testing significance of $X_4 = 0.11$	0.76	0.0001
FP	No	$971.44 - 2.05X_6 - 14.14X_2 - 33.45X_4 - 11.8X_7 + 8.06X_8$	0.97	0.0001
DUC	No	$205.67 - 7.96X_3 - 2.46X_7$	0.68	0.0001
VIS25	No	NO MODEL		
VISR25	No	NO MODEL		
VIS60	No	$(-48.722 + 1.758X_3 + 0.969X_4 + 0.958X_6) \times 10^3$	0.67	0.0002
VISR60	No	$2.66 - 0.04X_7$ P-value for testing significance of $X_7 = 0.10$	0.13	0.0001
RVIS135	No	$560 - 38.22X_2 + 49.68X_3 - 21.5X_5$	0.80	0.0001
VIS135	No	$-443.62 + 49.03X_4 + 16.39X_7$	0.55	0.0008
VISR135	No	$1.02 + 0.03X_8$	0.28	0.0126
PI	No	$-6.35 + 0.31X_3 + 0.13X_7$	0.74	0.0001
PTS	No	$0.05 - 0.001X_3 - 0.0006X_7$	0.77	0.0001
PR	No	$218.18 - 4.74X_3 - 4.14X_7$	0.63	0.0001
PVN	No	$-3.67 + 0.18X_4 + 0.038X_7$	0.63	0.0001
PVNI	No	$1.18 - 0.06X_6$	0.57	0.0001
VTS	No	$4.38 + 0.048X_3 - 0.1X_6$	0.43	0.0063
R	No	$2.132 + 0.17X_2$	0.76	0.0001
α_s	No	$8.32 \cdot 10^{-7} - 1.64 \cdot 10^{-7} X_2$	0.41	0.0025
T_s	No	No Model		
PEN25	Yes	$87.15 - 5.22X_5$	0.63	0.0021
SP	Yes	No Model		
G*@76	Yes	$31776 - 3300X_6$	0.44	0.0107
G*@80	Yes	$20516 - 2089X_6$	0.38	0.0344
S@-18	Yes	$-1207.3 + 66.6X_3 + 85.5X_6$	0.77	0.0006
S@-12	Yes	$-678.6 + 44.22X_3 + 40.04X_6$	0.70	0.0018
m@-18	Yes	$0.391 - 0.0114X_3$	0.46	0.0077
m@-12	Yes	$0.489 - 0.0158X_3$	0.52	0.0082

It is worth noting that the R^2 value for any model can be increased on the expense of entering variables that are correlated with ones already in the model or that are not significant, and this is one problem the stepwise procedure tries to avoid. For those variables with a very low R^2, for example VISR60 (an R^2-value of 0.13 for fresh samples and in fact no fitted model for aged samples), an explanation would be that either a linear model does not provide a good fit for the data or that there is really no relationship between the dependent variable, in this case viscosity ratio at 60°, and the independent variables, the molecular size distribution. The latter may well be the case, because in that regard a logarithmic transformation was done on the data for all the variables and different statistical procedures were run and the results are a lot like those from a linear model. As a matter of fact, for some there was a slight decrease in the R^2 value. On the other hand, a high value of R^2, for example 0.97 for the variable FP for fresh samples, may not necessarily mean that the given model represents the true relationship if there is no physical evidence to indicate that. This may just be a purely mathematical result with no physical evidence but may warrant further study. An important point that is worth noting is the non-uniformity in the models found for fresh and aged samples. By that, we mean for any variable the model fitted for fresh samples may differ in the number and the nature of the independent variables entered and thus in the magnitude of the regression coefficients and in the R^2 value. That may be attributed to the fact that aged samples are inherently different from fresh ones and thus molecular size distribution is different.

It should be noted that the physical properties of asphalts are measured on whole homogenized sample, whereas the R^2 values reported in Tables 5 and 6 are based on the regression analysis of randomly picked GPC fractions. We conclude by noting that although some of those models may look good, they should be examined carefully and interpreted in accordance with physical results.

CONCLUSION

Addition of polymers significantly improve the physical and rheological properties of Arab asphalts. HP-GPC characterization can be used to predict physical properties of asphalts and modified asphalts.

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