Crude Source Effects on the Chemical, Morphological, and Viscoelastic Properties of Styrene/Butadiene Latex Modified Asphalt Cements


The increasing costs and decreasing availability of good-quality asphalt cements across the United States has warranted the use of modifiers. Provided in this paper is a preliminary fundamental analysis of chemical variables (elemental analysis, molecular weight, functional group analysis, and chromatographic fractionation), microstructural effects as measured by scanning electron microscopy, and viscoelastic changes imparted by styrene butadiene latex addition as measured by dynamic, mechanical spectrometry. AC-10 and AC-20 asphalt cements from five crude sources representing a wide range of chemical and physical properties were chosen for this study.

CHEMICAL ANALYSES

Crude Sources

Two grades of asphalt cements from five sources were characterized in preparation for asphalt modifier studies. The asphalts were chosen to provide a wide range of composition for evaluating interactions between additives and asphalt components. Two asphalts originated from California, two from Texas, and one from Michigan. The following is a key to the sample abbreviations used throughout this paper, including the source where the sample was collected.

- California valley = CV-W,
- California coastal = CC-C,
- Texas = T-C,
- Texas = T-DS, and
- Michigan = MI-M.

Elemental Analysis

Elemental analysis results for the major nonhydrocarbon constituents are given in Table 1. Oxygen values have been calculated by differences and are therefore subject to more error than the others. There is good agreement between the sulfur and nitrogen levels from each source. Sulfur ranges from 0.8 to 6.8 percent and nitrogen from 0.5 to 1.16 percent by weight.

Metals Analysis

Table 2 gives the analytical results for major metals in the samples. No metals other than vanadium, nickel, and iron were detected at levels approaching 20 µg/g in any of the samples. In a few cases, low levels of zinc and copper were observed, but the presence of iron interfered with accurate quantitation. The asphalt samples were wet digested with nitric and sulfuric acids and analyzed by emission spectrometry with an inductively coupled plasma source.

Again, a wide range of vanadium, nickel, and iron concentrations are observed for the samples with C-CC AC-20 possessing the highest vanadium and nickel levels; T-DS AC-20 has the highest iron level, and T-DS AC-10 has the lowest vanadium and nickel concentrations. Some of the iron present in the samples may be attributable to processing during refining operations.

| TABLE 1 ASPHALT CEMENT ELEMENTAL ANALYSIS RESULTS (PERCENT BY WEIGHT) |
|--------------------------|---|---|---|
| AC Sample    | % N | % O | % S |
| CV-W AC10    | 1.16 | 0.9 | 1.56 |
| CV-W AC20    | 1.14 | 1.0 | 1.47 |
| CC-C AC10    | 0.96 | 0.4 | 6.19 |
| CC-C AC20    | 0.93 | 0.1 | 6.84 |
| Ml-M P85     | 0.60 | <0.1 | 4.02 |
| Ml-M AC20    | 0.82 | 0.5 | 3.72 |
| T-C AC10     | 0.47 | 0.1 | 4.02 |
| T-C AC20     | 0.48 | 0.1 | 3.96 |
| T-DS AC10    | 0.46 | <0.1 | 0.80 |
| T-DS AC20    | 0.46 | 0.21 | 0.87 |
TABLE 2 ASPHALT CEMENT METALS ANALYSIS (PARTS PER MILLION)

<table>
<thead>
<tr>
<th>AC Sample</th>
<th>Vanadium</th>
<th>Nickel</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC-C AC10</td>
<td>283</td>
<td>154</td>
<td>34</td>
</tr>
<tr>
<td>CC-C AC20</td>
<td>358</td>
<td>194</td>
<td>28</td>
</tr>
<tr>
<td>MI-M P85</td>
<td>216</td>
<td>68</td>
<td>17</td>
</tr>
<tr>
<td>MI-M AC20</td>
<td>213</td>
<td>70</td>
<td>16</td>
</tr>
<tr>
<td>T-C AC10</td>
<td>108</td>
<td>50</td>
<td>98</td>
</tr>
<tr>
<td>T-C AC20</td>
<td>98</td>
<td>50</td>
<td>162</td>
</tr>
<tr>
<td>CV-W AC10</td>
<td>57</td>
<td>112</td>
<td>50</td>
</tr>
<tr>
<td>CV-W AC20</td>
<td>56</td>
<td>124</td>
<td>89</td>
</tr>
<tr>
<td>T-DS AC10</td>
<td>22</td>
<td>24</td>
<td>285</td>
</tr>
<tr>
<td>T-DS AC20</td>
<td>23</td>
<td>27</td>
<td>440</td>
</tr>
</tbody>
</table>

Percent Aromatic Content

To obtain percent aromaticity in each asphalt cement, about 1 g was dissolved in 3 cm³ of deuterated chloroform and examined by carbon-13 nuclear magnetic resonance using a Bruker WM 360 instrument.

Percent aromaticity was calculated by dividing the aromatic carbon integrated area by the total carbon integrated area. The results in Table 3 indicate that the T-C and CV-W samples have significantly higher aromatic contents than do the CC-C or T-DS asphalt cements.

Apparent Molecular Weight Distribution

To gain an understanding of the relative molecular weight distributions of the asphalt cement samples, they were dissolved in tetrahydrofuran (THF) and separated by size exclusion chromatography (SEC) on a series of Varian Micropak, TSK columns. Both refractive index and ultraviolet absorption detectors at 340 nm were used. A broad molecular weight polystyrene standard was used to calibrate the instrument.

In Table 4, the apparent average (Mz), weight average (Mw), and number average (Mn) molecular weights are given. Mz is influenced by the higher molecular weight components in the distribution, whereas Mn is more affected by the lower molecular weight components in the distribution.

Again, there is good correlation between results for the two grades from each crude source. Except for T-DS, there is not much difference in Mn molecular weights among crude sources; however, the Mz and Mw data indicate that there are significantly more of the larger sized species in the T-DS and CC-C asphalts.

It must be emphasized that the SEC data provide only relative molecular size distributions. The size distributions are not absolute for two reasons. First, the size per unit weight of the polystyrene calibration standard does not duplicate that of the asphalt molecules; and, second, it is well known that the more polar asphalt molecules tend to associate in THF and that these associations behave as much larger species on the SEC column.

Infrared Spectroscopy and Functional Group Analysis

Infrared spectroscopic analyses have been performed on both asphalt concrete grades of all five asphalts. Spectra were obtained as 5 percent solutions in CS₂ to observe fingerprint absorption bands and sulfoxide levels. Functional group analyses based on selective chemical reactions and differential infrared spectroscopy were also performed. Results have been tabulated and are given in Table 5.

Ketones and anhydrides were virtually absent in the asphalt cements, which is expected because these functionalities are not native to the asphalt but are formed during atmospheric oxidative aging. Small amounts of oxidation are apparent in some samples as indicated by sulfoxide contents. Sulfoxides are oxidation artifacts formed from sulfide oxidation and are the most easily formed oxidation functionality in asphalts.

Note: Mz = apparent average, Mw = weight average, and Mn = number average.
Carboxylic acids were found in significant amounts only in California asphalts with the amounts in the CV-W asphalt being greater than twice those in the CC-C asphalt. Further, most of the acids in the CV-W asphalt are present as carboxylate salts, suggesting caustic treatment of the crude during refining, which concentrates acid components in the asphaltic residue. The 2-quinolone types are naturally occurring and their relative concentration is a characteristic of the crude source. This compound type is important because it forms strong hydrogen-bonding dimers with itself and mixed, hydrogen-bonding dimers with carboxylic acids. These association reactions are important to asphalt physical properties and aging characteristics.

Several characteristic absorption bands are useful for fingerprinting asphalt and obtaining information about important hydrocarbon characteristics. The peak intensities for the absorption bands, together with the functional group analyses, confirm that the AC-10s and AC-20s from each refinery source were manufactured from the same crude oil source or blend.

Of particular interest is the high absorptivity of the 1600-cm\(^{-1}\) band of the CV-W asphalt compared with the other asphalts. The 1600-cm\(^{-1}\) band arises in unoxidized asphalts primarily from C = C stretching of aromatic ring systems with smaller contributions from the C = N of aromatic ring systems, which include the pyridine moiety. The apparent aromaticity differences may relate to the differences in the phase morphologies of the dispersions of styrene/butadiene (S/B) latex between the CC-C and CV-W asphalts, as can be observed in the photomicrographs shown later in this paper.

The more aromatic CV-W asphalt probably contains components that are better solvents for S/B latex and thus impart the visual appearance of partial solubility or compatibility with the asphalt to the dispersed latex in the CV-W asphalt. The increased interaction between the CV-W asphalt and S/B latex probably also accounts for the enhanced response of the CV-W asphalt to physical property improvements (temperature and shear susceptibility) compared with the CC-C asphalt, as evidenced by viscoelastic data that will be presented later in this paper.

**Asphalt Fractionation**

Asphalt cement samples were fractionated according to ASTM method D4124. In this procedure, the asphaltenes are precipitated from the asphalt by the nonpolar solvent heptane. The heptane solution is then percolated through an alumina column and the fractions displaced with increasingly polar solvent systems. The most weakly adsorbed saturates fraction is removed with heptane, the naphthene aromatics fraction with benzene, and the polar aromatics fraction with methanol-benzene followed by trichloroethylene. Although the names of the fractions were intended to suggest the major compositional types present, each fraction is still a highly complex mixture of chemical compounds and the same generic fraction from different asphalts can vary widely in composition.

It can be observed from the data in Table 6 that the component analyses vary considerably from one asphalt to another, indicating significant differences in chemical composition or polarity of the molecular components. The increased solvent power of the CV-W asphalt for the S/B latex is further understood from its reduced asphaltene content and increased amounts of aromatic fractions compared with the CC-C asphalt. T-DS asphalt cement also stands out as one containing virtually no asphaltenes and a high concentration of polar

**TABLE 5 INFRARED SPECTROSCOPIC ANALYSIS OF UNMODIFIED ASPHALTS***

<table>
<thead>
<tr>
<th>Source</th>
<th>Grade</th>
<th>Ketones</th>
<th>Anhydrides</th>
<th>Carboxylic Acids</th>
<th>2-Quinolone Types</th>
<th>Sulfoxides</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Free</td>
<td>Salts</td>
<td>Total</td>
</tr>
<tr>
<td>CC-C</td>
<td>AC-10</td>
<td>0</td>
<td>0</td>
<td>0.027</td>
<td>0</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>AC-20</td>
<td>0</td>
<td>0</td>
<td>0.014</td>
<td>0.002</td>
<td>0.016</td>
</tr>
<tr>
<td>CV-W</td>
<td>AC-10</td>
<td>0</td>
<td>0</td>
<td>0.002</td>
<td>0.058</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>AC-20</td>
<td>0</td>
<td>0</td>
<td>0.005</td>
<td>0.048</td>
<td>0.048</td>
</tr>
<tr>
<td>T-C</td>
<td>AC-10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>AC-20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T-DS</td>
<td>AC-10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>AC-20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MI-M</td>
<td>P-85</td>
<td>0</td>
<td>0</td>
<td>Trace</td>
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</tr>
<tr>
<td></td>
<td>AC-20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Asphalt as 5% solution in CS\(_2\), 1 mm cell thickness.

\(^b\)Difference in the two values caused by variable intensity of shoulder band at 1650 cm\(^{-1}\).
aromatics. In addition to being deficient in material precipitated by heptane (the asphaltenes may be highly dispersed in heptane and thus pass the filter), T-DS asphalt cement is also deficient in nonpolar materials that would be found in the saturated fractions.

As can be observed from the data in Table 6, there is some loss during the analysis, primarily from strongly adsorbed components that are not desorbed from the alumina column. These components are probably most nearly similar to those components found in the polar aromatics fraction.

EFFECT OF CRUDE SOURCE AND GRADE ON LATEX PHASE MORPHOLOGY

Experimental

The latex-asphalt cement blends were prepared in the following manner for all of the asphalt crude sources. About 2 gal of each asphalt cement were weighed and heated to between 280°F and 300°F while stirring using a Lightnin mixer with a two-blade impeller. Enough S/B latex (DOWNRIGHT HM-100L from The Dow Chemical Company) was added slowly to make a mix of 5 percent in asphalt cement (based on asphalt cement). [DOWNRIGHT HM-100L latex is a water-based emulsion (70 percent) made up of 24 percent styrene/76 percent butadiene polymer. DOWNRIGHT is a trademark of The Dow Chemical Company.] The mixture was then placed in an oven at 280°F until a constant weight was obtained. This mixture was then broken down into 1-qt aliquots and allowed to cool.

To prepare asphalt cement samples for microscopic examination, 5-mm³ samples of the latex modified asphalt were put into a 25-mL glass-stoppered Erlenmeyer flask and 15 mL of methyl ethyl ketone-osmium tetroxide (2 percent fixing solution) was added. The mixture was allowed to stand for at least 12 hr for complete fixing of the latex and dissolution of the asphalt by the methyl ethyl ketone (MEK). Then the dissolved asphalt and MEK were pipetted from the flask and the sample washed three times with reagent grade MEK. The remaining fixed latex structure was cross sectioned with a razor blade and vacuum dried for 10 min at room temperature. The cross-sectional surfaces of the sample were mounted on scanning electron microscope (SEM) stubs with silver conductive paint and coated with gold approximately 200 Å thick. Examination and photomicrography were done with a Hitachi S-520 scanning electron microscope.

Results

The morphological characteristics of latex in asphalt cements were found to vary widely, depending on crude source. Figures 1–10 show electron micrographs of 5 percent S/B latex in AC-10 and AC-20 samples. Five distinctly different structural networks are shown in these photographs: fine and coarse continuous strings (Figures 1, 2, and 5); open cells (Figures 4 and 6); closed cells (Figure 7); sheetlike, thin films (Figure 8); and thick, discontinuous fibrils (Figures 9 and 10).
Several observations can be made from the photographs. Prediction of observed microstructure within the same crude source cannot always be reliably made based on microstructure information from one grade of asphalt cement. With the exception of Figures 1 and 2, there are virtually little or no similarities between the latex microstructures observed in AC-10s and AC-20s from all crude sources. Also, across the crude source range studied, significant differences in latex microstructure are observed among AC-10s and among AC-20s. It would be expected that this aspect of asphalt modification has a significant bearing on the level of property performance improvement across crude source types and grades. A fundamental understanding of the relationship between latex microstructure in asphalt cements and actual field performance properties may indicate that one type of microstructure is preferred over another for optimal results. Methods for custom tailoring additive systems that would result in the desired microstructure could then be investigated.

In conclusion, crude source has a definite influence on the latex phase morphology, as demonstrated by SEM studies. The mode of mixing latex in the asphalt may also influence latex microstructure. SEM appears to be a good analytical tool for rapidly studying latex modifier distribution and morphology in a large number of asphalt crude sources and grades. The ultimate long-term impact of these studies may result in custom tailoring asphalt additives for specific needs to optimize pavement performance.

VISCOELASTIC EVALUATION OF S/B LATEX MODIFIED ASPHALT CEMENTS

Experimental

The viscoelastic properties of neat and modified asphalt cement were measured using a Rheometrics Model 605 Mechanical Spectrometer. Data were taken over a three-decade range (from 0.1 to 100 radians per sec) at 10°C intervals from -20°C to +60°C. Parallel plate geometry was used, employing 8-mm plates from -20°C to +20°C, and 25-mm plates from +30°C to +60°C. Sample thickness was typically 1 mm.

Data Handling

Primary data in these evaluations are typically $G'$ (storage modulus), $G''$ (loss modulus), temperature, and frequency. After the mechanical portion of the testing was completed, the primary data were transferred to a VAX 11/780 for further manipulation. After transfer, the data were shifted to form a single master curve using 0°C as the reference temperature. Figure 11 shows one example of the shifted modulus values for CC-C asphalt cement.

After shifting, the dynamic viscosities were calculated according to the following equation:

$$\eta^* = \sqrt{(G')^2 + (G'')^2}/W$$

where $\eta^*$ is the dynamic viscosity and $W$ is the shifted frequency. Figure 12 shows dynamic viscosity results for neat CV-W and CC-C asphalt cements, and Figure 13 shows dynamic viscosities for S/B latex modified asphalt cements. The interpretation of the results from these graphs is as follows.

Perhaps the most revealing values from viscoelastic analysis are the loss tangents, that is,

$$\tan \delta = (G'')/(G')$$

where $\tan \delta$ is the loss tangent. Figure 14 shows shifted values for CC-C AC-10 asphalt cement neat and with 5 percent latex. The significant increase in elasticity at low frequency (equivalent to high temperature) on the addition of modifier is apparent.

$\tan \delta$ data can also be plotted as a function of temperature. Figure 15 shows results analogous to those shown in Figure 14. As a result, either method can be used to display viscoelastic phenomena because low frequency is equivalent to high temperature when viscoelastic effects are being measured.

Results

Viscoelastic analysis can be used in a number of ways to interpret the behavior of neat and modified asphalt cements. First, the data can be used to provide important information on materials. Figures 12 and 13 show that the CC-C asphalt cements have viscosities that are much higher than those of CV-W asphalt. However, on the addition of a modifier, the two sources give viscosity profiles that are nearly the same, indicating that the effect of the additive on viscosity is greater in the CV-W asphalt cement than in the CC-C asphalt cement.

Second, these data can be correlated with other properties. For example, the loss tangent master curves at low frequency (Figure 16) can be used to differentiate between additives. In this case, they correlate well with ductility performance because modified asphalt cements with lower values of $\tan \delta$ have better low-temperature ductility. More important than the correlation is the existence of an independent parameter from which a mechanism of improvement can be inferred, that is,
FIGURE 11 Shifted data (0 degrees) for 0-CC-C AC-10.

FIGURE 12 Dynamic viscosities for neat CV-W and CC-C asphalt cements.
FIGURE 13 Dynamic viscosities for S/B latex modified asphalt cements.

FIGURE 14 Loss tangent data for CC-C AC-10.
FIGURE 15  Loss tangent data for CC-C AC-20 as a function of temperature.

FIGURE 16  0°C loss tangent master curves at low frequency for modified asphalt (AC-10) with different ductilities (39°F).
ductility may be the result of elasticity at low frequencies (strain rates).

Third, a viable technique exists for providing insight into the effective compatibility of a mixed system. For example, in Figure 15 the presence of additive causes a decrease in TAN D; however, even with the additive, TAN D is a smoothly increasing function of the temperature. In contrast, Figure 17 shows a case in which the additive produces a TAN D curve that has a sigmoidal character. These rather distinct differences can be traced to differences in the interaction between the asphalt cement and the additive; there is probably a difference in the dispersion or swelling of the additive in the two cements.

CONCLUSIONS

Dynamic mechanical spectroscopy is being used to evaluate performance of additives to various asphalt cements. Visous behavior can be evaluated either during application or in use. Dynamic data can be used to correlate with other tests and also to infer mechanisms by which additives interact with various asphalt cements.

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