

Quantitative Determination of Polymers in Asphalt Cements and Hot-Mix Asphalt Mixes

CHRISTINE W. CURTIS, DOUGLAS I. HANSON, SHOU TA CHEN, GUEI-JEN SHIEH,
AND MEI LING

The addition of polymers in asphalt cement has been widespread. Quantitative analysis of these polymers is essential to verify if specifications are being met. The analysis of two styrene butadiene rubber (SBR) latexes and ethylene vinyl acetate (EVA) and styrene butadiene styrene (SBS) polymers in three different asphalts was accomplished by Fourier transform infrared (FTIR) spectroscopy. Although the behavior of each SBR latex in each asphalt yielded somewhat different calibration curves, each latex-modified asphalt cement was successfully quantified. The values for latex determined by FTIR spectroscopy yielded a more linear relationship between the dynamic shear measurements and the latex concentration than the nominal values that accompanied the mixtures. Both EVA and SBS polymers were also quantified by using the analysis that was developed for the SBR latex-modified asphalt. The infrared analysis of SBR latex in asphalt was directly applied to the analysis of SBR latex in asphalt-aggregate mixes. Analysis of 3 weight percent SBR latex in asphalt concrete samples was achieved by removing the SBR latex-modified asphalt from aggregates and analyzing the latex content by FTIR spectroscopy. Three different aggregate types, gravel, granite, and limestone, were used.

In recent years the Alabama Department of Transportation has made extensive use of styrene butadiene rubber (SBR) latex as a modifier for asphalt cement. It has specified the material to provide a binder that would provide enhanced performance in the field in terms of rutting resistance, fatigue resistance, and stripping resistance. The department's specification for latex-modified asphalt cement was a recipe type specification, which called for the addition of 3 percent SBR latex to an asphalt cement (generally an AC-20 asphalt cement). In general, until very recently SBR latex was added to the asphalt cement at the contractor's hot-mix asphalt (HMA) plant. The Alabama Department of Transportation had to rely on the supplier and the contractor to ensure that the specified amount of modifier had been added to the asphalt cement. The department did not have the capability to verify independently that the correct amount of SBR latex had been added to the asphalt cement. Thus, there was a need to develop such a capability.

OBJECTIVE

The objectives of the present study were to evaluate existing procedures and develop a readily usable procedure for determining the

percent latex in asphalt cement for use by the Alabama Department of Transportation. Another objective was to apply this method with appropriate modifications to determine the amount of latex in HMA mixes.

SCOPE

The study evaluated the use of Fourier transform infrared (FTIR) spectroscopy as a method for determining the percent latex in asphalt cement and HMA. The study was accomplished with two different SBR latexes from Ultrapave, UP70 and UP2897, and three different asphalt cements that are routinely supplied to roads in the state of Alabama. Three different aggregates were used. These aggregates are produced in Alabama and are routinely used in Alabama's pavements. The scope of the objectives was also expanded to two other polymers, ethylene vinyl acetate (EVA) and styrene butadiene styrene (SBS) copolymer. In this research SBR latex was analyzed both qualitatively and quantitatively in asphalt cement so that both the presence and amount of latex present in the asphalt cement were successfully determined. The procedure that was developed for analyzing the latex in asphalt cement was applied to latex-modified asphalt concrete with four different aggregates. Asphalt modified with 3 percent SBR latex was first added to aggregates, removed with tetrahydrofuran (THF), and then analyzed for SBR latex content by using the calibration curves obtained previously. The procedure for analyzing SBR latex in asphalt cement was then applied to EVA- and SBS-modified asphalt cement.

BACKGROUND

Polymers are added to asphalt cement to improve the performance characteristics of the asphalt cement. Properties that the addition of these materials is seeking to improve are temperature susceptibility, cohesive strength, elastic recovery, and adhesive power or tackiness (1). The polymer-modified asphalt cement must be able to maintain its desirable characteristics during storage and service life, be chemically and physically stable and usable through all aspects of processing, and be cost-effective.

A number of different methods have been used to determine the amount of SBR latex in asphalt. Lenoble (2) used microscopic techniques with UV fluorescence reflection to determine if natural segregation occurred with two incompatible polymers, a polyolefin and SBS, in several different asphalts. Lenoble (2) determined that the

C. W. Curtis, Department of Chemical Engineering, Auburn University, Auburn, Ala. 36849. D. I. Hanson, National Center for Asphalt Technology, 211 Ramsay Hall, Auburn University, Auburn, Ala. 36849-5354. S. T. Chen, G.-J. Shieh, and M. Ling, Auburn University, Auburn, Ala. 36849.

polydispersity of the phases and the fineness of the SBS dispersion were influenced by blending conditions, asphalt composition, and aging susceptibility. Similarly, Paukkau et al. (3) used an automated morphological analysis system to analyze polymer-modified asphalt materials. The system was composed of a scanning electron microscope with a television camera. Another method, gel permeation chromatography, was used successfully to determine the low-gel polymer content in polymer-modified asphalt and tar (4).

Of all of the methods reviewed, methods that use infrared (IR) spectroscopy for analyzing latex in asphalt appear to be the most practical and widely used. IR spectroscopy is both accurate and relatively simple to perform. When IR radiation is imposed on a sample the amount of light that is either transmitted or absorbed is measured typically over a nominal wavelength range of 4000 to 400 cm^{-1} . Unique spectra are obtained for different compounds since each functional group absorbs at specific wavelengths and produces a unique fingerprint in the region from 1500 to 400 cm^{-1} because of long-range molecular interactions. The IR spectrum of a mixture such as asphalt cement represents the IR absorbances of all of the compounds present, yielding a sum of the individual absorbances. When asphalt cement is considered as a single entity, then the addition of another material such as a polymer is apparent in the IR spectrum if the IR absorbances from the polymer's molecular bonds are distinct from those in asphalt and are IR active.

IR spectroscopy is a powerful technique and has been successfully applied to the analysis of asphalt (5,6). Polymers themselves have also been extensively analyzed by IR spectroscopy (7,8). An ASTM procedure for the analysis of polymers in asphalt that uses IR spectroscopy was developed by Choquet and Ista (9). For the three polymers used, the method was successful for the SBS latex- and EVA polymer-modified asphalt binders tested. The third polymer, atactic polypropylene, had to be subjected to an intensive separation procedure before analysis.

The two IR methods that are discussed here were the two that served as starting points for the study. The test procedures were TEX 533-C, Determination of Polymer Additive Percentages in Polymer Modified Asphalt Cements (10,11), from the Texas State Highway Department and AHTD Test Method 432, Test for Polymers in Asphalt, from the Arkansas State Highway Department (12). The Arkansas method (12) for determining polymers in asphalt was very similar to the Texas method except that 1,1,1-trichloroethane rather than THF was used as the solvent.

The Texas State Department of Highways and Public Transportation's Materials and Tests Division developed a methodology for determining the percentage of polymer additives in polymer-

modified asphalt cements (10,11). The particular additives that were targeted in their procedure were SBR latex, SBS block copolymer, ethylene acrylic acid, and EVA. These polymers were analyzed in polymer-modified asphalt cements. The procedure involved the use of IR spectroscopy to develop calibration curves from asphalt standards containing 1, 2, 3, 4, and 5 percent polymer (by weight) and then tested the unknown polymer-asphalt samples to determine the amount of polymer present in the asphalt. Standards were prepared from hot asphalt at 160°C at (320°F). The polymer-modified asphalt samples analyzed by IR analysis were prepared by placing a THF solution of the polymerized asphalt on a salt plate, evaporating the THF, and allowing the thin film to solidify. This method only worked when the polymers were soluble in THF. When the polymers were not soluble in THF, a hot melt of dispersed polymer in asphalt was made and the hot melt was spread as a thin film onto the salt plate.

Both types of samples were analyzed identically by setting the baseline transmission to 80 percent at 4000 cm^{-1} and scanning the sample from 4000 to 600 cm^{-1} . The calibration curves were analyzed by obtaining the ratio of the relative peak height of the IR peak of the polymer to that of the IR peak of the asphalt cement. For SBR latex the IR peak of interest is at 965 cm^{-1} (A1), and for asphalt the peak is at 1375 cm^{-1} (A2). Baselines were drawn at the peaks of interest, and the peak heights A1 and A2 were measured. The ratio of peak height A1 to peak height A2 was calculated and was used to plot the polymer concentration versus the A1/A2 ratio. The unknown samples were prepared by the same procedure used to prepare the calibration curve. The calibration curve was used to determine the concentration of the unknown.

TEST PLAN

Materials

The materials used in the present study were three different asphalts from Coastal, Hunt, and Ergon; SBR latexes; and EVA and SBS polymers. The crude source for Coastal asphalt was Venezuelan crude, that for the Hunt asphalt was Mexican crude, and that for Ergon asphalt was sour Venezuelan crude. The SBR latexes used were obtained from Ultrapave and are designated UP70 and UP2897. The characteristics of these latexes are given in Table 1. The latex-modified asphalt cement samples used for calibration were prepared by Ultrapave at nominal concentrations ranging from

TABLE 1 Properties of Polymers

Properties	Polymer	
	UP 2897	UP 70
Solids Content, %	68.0 ± 5.0	70.0
pH	9.5-10.5	10.0
Viscosity, Brookfield, cps	1200-1500	1650
Weight per Gallon, lbs	7.95 ± 0.3	7.9
Density, kg/L	0.9526	0.9466
Styrene Butadiene Ratio	24:76 ± 2.0	24:76

0.5 to 8.0 weight-percent latex in asphalt. Bulk samples were also prepared by Ultrapave at nominal concentrations of 2, 3, and 4 weight-percent latex in asphalt. The characteristics of these latex-modified asphalt cements are given in Table 2.

The EVA polymer, EVA in asphalt cement samples, and SBS in asphalt cement samples were obtained from Exxon; another set of SBS in asphalt cement samples was obtained from Koch. The EVA-modified and the SBS-modified asphalt cement samples were prepared at concentrations of 2, 3, and 4 weight-percent in the three asphalts mentioned previously. The characteristics of these polymers are also given in Table 1.

The aggregates used in the present study in conjunction with the asphalt containing latex were a 1.3-cm (0.5-in.) open-graded and

dense-graded Mt. Meigs gravel from Montgomery, Alabama. These materials have very low absorptions. Two other aggregates were also used: a dense-graded limestone from Dravo, Auburn, Alabama, and a dense-graded granite from Columbus or LaGrange, Georgia. The gradation of the aggregate ranged from 0.075 to 19 mm, with 0.075- to 2.36-mm aggregates composing one-half of the material.

IR Analysis of Latex in Asphalt Cement: Experimental Procedure

IR analysis of SBR latex in asphalt cement was performed with an FTIR spectrometer (Nicolet 5SXC). The IR cells used were single

TABLE 2 Properties of Latex-Modified Asphalt Cements

Asphalt Binder	Latex		Penetration		Capillary Viscosity		Softening Point
	Type	%	39°F	77°F	Absolute 140°F (P)	Kinematic 275°F (cSt)	°C
Coastal	None	0	22	78	2357	394	117.0
Coastal	UP2897	2	24	74	3411	704	125.0
Coastal	UP2897	3	23	64	4608	916	126.0
Coastal	UP2897	4	26	57	16518	2790	138.0
Coastal	UP70	2	24	65	5067	779	128.0
Coastal	UP70	3	23	48	8484	1264	132.0
Coastal	UP70	4	25	70	11453	1781	138.0
Ergon	None	0	21	72	2118	370	118.0
Ergon	UP2897	2	23	76	3148	647	122.0
Ergon	UP2897	3	22	60	4482	850	125.0
Ergon	UP2897	4	23	52	8263	1926	132.0
Ergon	UP70	2	24	68	5951	1092	127.0
Ergon	UP70	3	24	57	7035	1069	129.0
Ergon	UP70	4	57	87	8629	1597	133.0
Hunt	None	0	25	71	2273	475	122.0
Hunt	UP2897	2	28	61	3119	793	124.0
Hunt	UP2897	3	23	66	6739	1228	131.0
Hunt	UP2897	4	28	59	8943	2941	140.0
Hunt	UP70	2	28	57	5249	1076	129.0
Hunt	UP70	3	30	66	5867	1183	131.0
Hunt	UP70	4	54	82	11483	2362	136.0

sodium chloride salt plates mounted in a holder. The salt plates and holder were obtained from Harrick Scientific. While in use the spectrometer was purged with dry nitrogen to remove the CO_2 and water in the ambient air. Desiccant was also placed in the spectrometer to absorb any moisture that may seep into the spectrometer. Asphalt samples containing different amounts of SBR latex, 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 6.0, and 8.0 weight-percent latex in asphalt, were prepared by Ultrapave. THF was used as the solvent and was high-pressure liquid chromatographic grade from Fisher Scientific.

The method used for analysis of SBR latex in asphalt was a modification of test method TEX 533-C from the Texas State Department of Highways and Public Transportation (11). The procedure used IR spectroscopic determination of the IR bands corresponding to latex at 965 cm^{-1} and to asphalt at 1375 cm^{-1} . The 965-cm^{-1} latex band (A1) is attributed to $=\text{C}-\text{H}$ in phase out-of-plane bending of *trans*-1,4-butadiene in SBR latex (13). The IR absorption band at 1375 cm^{-1} (A2) corresponds to $\text{C}-\text{CH}_3$ deformation of aliphatic compounds in asphalt (13). The presence of the 965-cm^{-1} band in the asphalt IR spectrum indicated the presence of SBR latex in the asphalt since that absorption was not present in the virgin asphalts. The ratio of absorbance bands, A1:A2, was used as the quantitative method.

The general procedure for obtaining the analysis is given in the following description. Before analysis a background spectrum of the NaCl salt plate and spectrometer atmosphere was obtained. A sample was prepared from each latex-modified asphalt cement by dissolving 10 weight-percent of the latex-modified asphalt cement in THF. A thin film of latex-modified asphalt was prepared on an NaCl salt plate by placing 0.3 ml of solution on the salt plate and spreading the solution evenly over the surface of the salt plate. Most of the THF evaporated during the process, since the sample was prepared in the fume hood. The thin film was then dried in an oven at 60°C for 20 min to evaporate the THF completely. The salt plate was removed from the oven and was allowed to cool for 5 min. The sample was then analyzed by FTIR spectroscopy. Each sample on a salt plate was analyzed 3 times by rotating the plate 120 degrees for each analysis. Averaging the three ratios allowed the effect of any unevenness in the sample to be minimized. The absorbance of the 1375-cm^{-1} peak normally fell between 0.35 and 0.65 absorbance units, although slightly higher or lower absorbances gave satisfactory results. A tangent-line baseline method was used to calculate the absorbance of the analytical bands.

Calibration Curves

Calibration curves of latex-modified asphalt cement containing 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 6.0, and 8.0 weight-percent latex were obtained by using the combinations of Hunt, Coastal, and Ergon asphalts with Ultrapave latexes UP70 and UP2897. These calibration standards were prepared in bulk and were sampled after preparation by placing several drops in a sample vial. Each asphalt was combined with each latex yielding six combinations of latex-modified asphalt cement. The calibration curves were developed for each combination and are given in Figure 1. Each analysis was duplicated. Although the calibration curves were similar to each other, the characteristics of the SBR-asphalt combination varied sufficiently in terms of the linear relationship between SBR concentration and area ratio that each latex-modified asphalt required a separate calibration curve.

IR Analysis of EVA and SBS

The same experimental procedure that was used for SBR latex in asphalt was applied to asphalt samples containing EVA and SBS. The IR absorbances used in the analysis of EVA were 1242 cm^{-1} (h_1), which is attributable to $\text{C}-\text{O}-\text{C}$ in acetate, and 1736 cm^{-1} (h_2), which is attributable to $\text{C}=\text{O}$ in acetate (13). These absorbances are unique for EVA and are not present in the asphalt spectrum. The ratio of each of these two peaks against the 1375-cm^{-1} peak from asphalt was determined. Analyses of EVA at three concentrations in each of the three asphalt cements were performed. Since SBS contains the same monomers as SBR latex, a similar IR spectrum is obtained. The SBS peak of interest was at 966 cm^{-1} , which is attributable to the $=\text{C}-\text{H}$ bend in *trans*-1,4-butadiene. The ratio of each of these peaks against the 1375 cm^{-1} asphalt peak was determined. The SBS polymer from two different suppliers was also analyzed at three concentrations in each of the three asphalt cements.

ANALYSIS OF RESULTS

Applicability of Analysis Method for Latex-Modified Asphalt

Figure 2 presents the FTIR spectra of virgin asphalt and asphalts that contain SBR latex, EVA, and SBS. The characteristic peak for each polymer and for asphalt is marked on the spectrum. The calibration curves prepared from the SBR latexes in asphalt cement provided a means by which to analyze the SBR latex contents in these three asphalts. These calibration curves are presented in Figure 1; the solid circles represent the SBR latex concentration-versus-peak area data. The R^2 values for these calibration curves were 0.99 for SBR latex (UP2897 and UP70)-modified Coastal and Ergon asphalts. The R^2 value for UP2897 in Hunt asphalt was also 0.99, whereas the UP70 latex in Hunt asphalt gave a R^2 value of 0.98. Hence, two different latexes were successfully quantified in three different asphalts, which confirmed the applicability of the method to a variety of materials and to a concentration range of from 0 to 8 weight-percent of SBR in asphalt.

An example of the applicability and usefulness of this technique for analysis of the amount of latex present occurred in a project in which the storage of latex-modified asphalt cement was being investigated by researchers at the National Center for Asphalt Technology (NCAT). Bulk samples of nominal, 2, 3, and 4 weight-percent SBR latex in Coastal, Hunt, and Ergon asphalts were prepared for NCAT by Ultrapave. These samples were prepared in the laboratory by using laboratory quantities; the preparation procedures were, however, similar to those that would be used for introducing SBR latex into asphalt cement for road construction. Researchers at NCAT performed physical tests on the samples of different concentrations and evaluated the effects of storage on these samples. For some of the samples the results from the physical tests did not appear to follow the nominal concentrations stated by Ultrapave. At that point the samples with nominal 2, 3, and 4 weight-percent SBR latex in asphalt were analyzed by FTIR spectroscopy by using the procedure and calibration curves developed for each asphalt and SBR latex combination. The concentrations of the laboratory-produced bulk samples were determined. The actual concentrations of the SBR latex in the asphalt bulk samples as determined by FTIR spectroscopy varied, in some cases considerably, from the nominal values. The results from the physical tests were in better agreement with the SBR latex concentrations determined

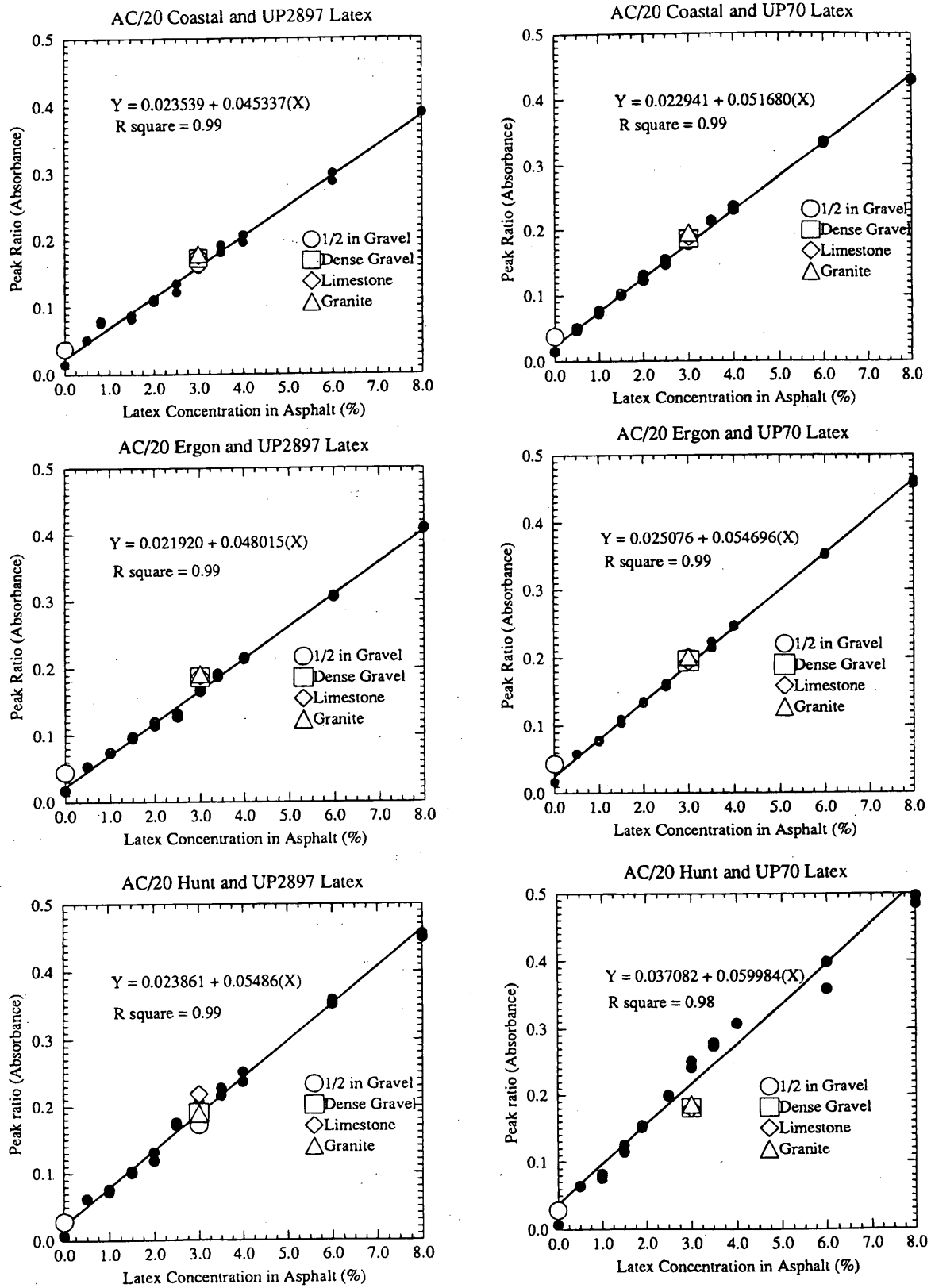


FIGURE 1 Calibration curves of SBR latex in asphalt and results from asphalt-aggregate mixes.

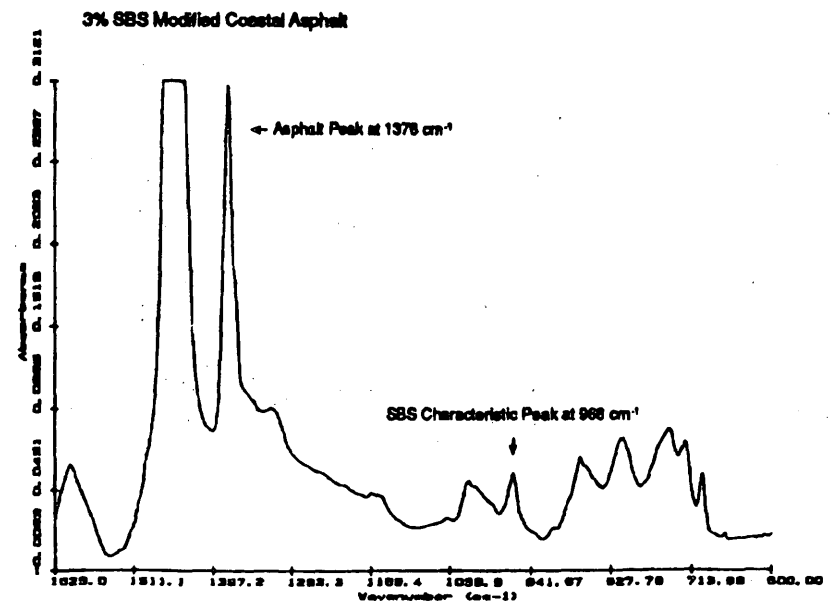
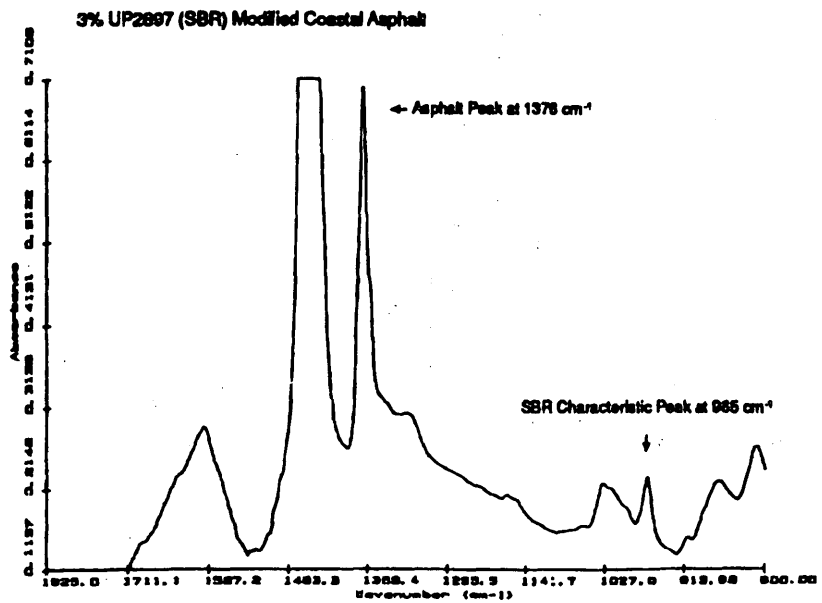
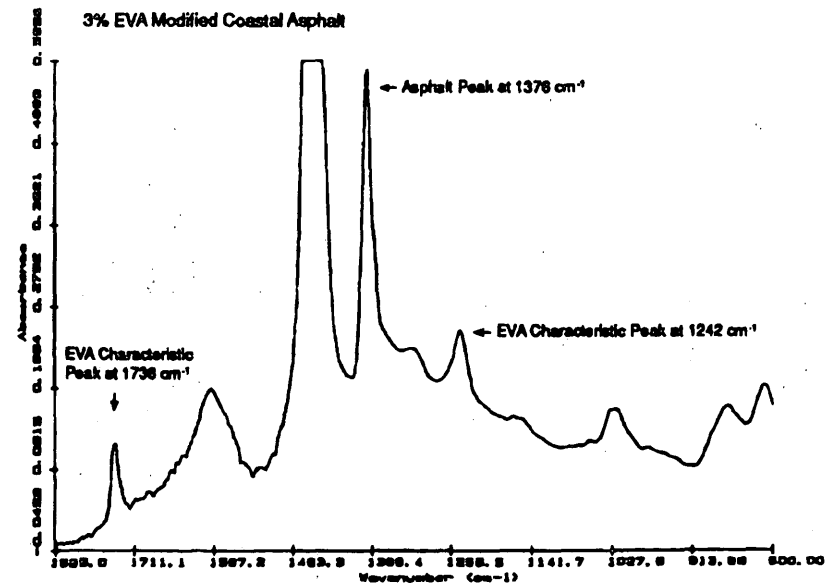
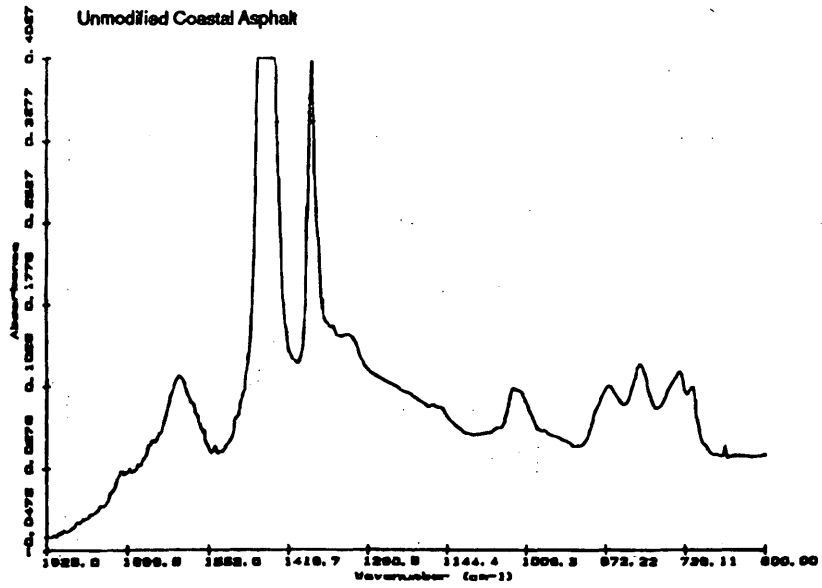


FIGURE 2 IR spectra of polymer-modified and virgin asphalts.

from the calibration curves than the nominal values, as shown in Figure 3 in which the dynamic shear, $G^*/\sin \delta$ (in kilopascals, where G^* is the complex shear modulus and δ is the phase angle) of the SBR latex-modified asphalt cement is compared with the latex concentrations determined by FTIR spectroscopy. The latex concentrations determined by FTIR spectroscopy yielded a more linear relationship between the dynamic shear measurement and the latex concentration for the SBR-modified Coastal and Ergon

asphalts than did the nominal values. The Hunt asphalt, which was produced from a Mexican crude, whereas the other two asphalts were produced from Venezuelan crudes, showed nonlinear behavior. SBR latexes are known to be incompatible with some Mexican crudes and tend to separate rapidly, which could explain some of the variability with the Hunt asphalt. The interaction between the SBR latex and the asphalt appeared to be dependent on the asphalt characteristics and the interaction between SBR latex and asphalt.

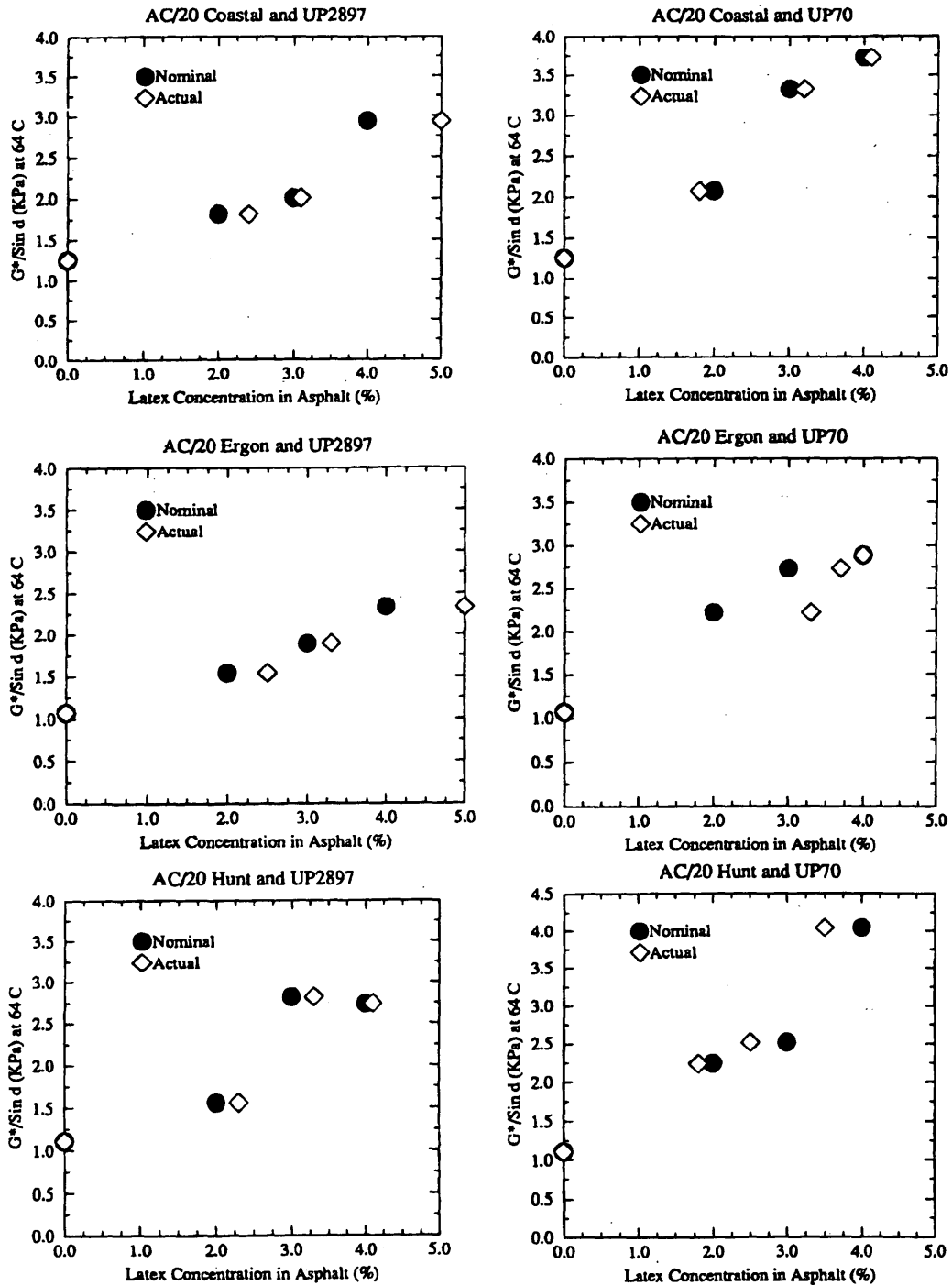


FIGURE 3 Relation between $G^*/\sin \delta$ and latex concentration in asphalt.

IR Analysis of Latex-Modified Asphalt in an Asphalt-Aggregate Mixture

A feasibility study was conducted to determine if the latex content of latex-modified asphalt could be accurately analyzed after the latex-asphalt mixture had been mixed with aggregate. The tests performed involved a gravel and a granite, which are siliceous, non-absorbing aggregates, and a limestone. Two different samples of the gravel were used: (a) 1.3-cm (0.5-in.) aggregates were coated with asphalt cement containing 3 weight-percent latex; a heavy coat of asphalt was applied so that the asphalt content was 8 percent of the mix; (b) a typical gradation of gravel was coated with 6 percent asphalt cement containing 3 percent latex; and (c) typical gradations of both limestone and granite were coated with 6 percent asphalt containing 3 percent latex. The asphalts used were Coastal, Ergon, and Hunt asphalts, and the latexes used were UP70 and UP2897, yielding six combinations. Baseline experiments in which the asphalt cements without latex were coated on the 1.3-cm (0.5-in.) aggregate were also performed.

For each of these asphalt-aggregate mixtures the asphalt cement was removed from the aggregate surface with THF. The sample was shaken with the THF for approximately 4 hr. The THF solution containing asphalt was then removed from the flask, centrifuged to remove any particulates from the aggregate, and analyzed as a thin film cast on an NaCl salt plate by FTIR spectroscopy. The presence of latex was detectable in the asphalt cement. The amount of latex present was quantitatively determined by using the calibration curves developed for the six combinations of asphalt and latex used

in the study. Figure 1 presents the analysis of the asphalt-aggregate mixtures containing latex-modified asphalt; the points representing the latex content of asphalt abstracted from aggregate are the open circles. Baseline results from samples that do not contain latex are also presented. The amount of SBR latex (3 percent) present in the asphalt cement was accurately determined for all four aggregates. SBR latex-modified Coastal and Ergon asphalts yielded results that closely agreed with the calibration curves. Calculation of the average difference from the calibration line for these two asphalts ranged from -0.0139 to -0.0876 . On the same scale the Hunt asphalt-UP70 sample yielded a larger difference of -0.1398 . The Hunt asphalt-UP2897 samples gave more scatter among the four latex-modified asphalts removed from the different aggregates, although the difference from the calibration curve was small (-0.0147). Hence, the SBR latex-modified Hunt asphalt yielded results that deviated from the calibration curve more than results for the other two latex-modified asphalts did.

To evaluate the reproducibility of the method for removing latex-modified asphalt cement from aggregate, these analyses were performed by two different researchers. The analyses for open- and dense-graded gravel were performed by both Researcher 1 and Researcher 2. Researcher 1 had developed the technique, whereas Researcher 2 performed the analysis from the written procedure. Since both researchers obtained 3 weight-percent latex in all of the samples analyzed (Table 3), the procedure developed appears to be insensitive to operator variability. After the reproducibility was established Researcher 2 proceeded to perform the analysis of SBR latex-asphalt mixes of limestone and granite as presented in Figure 1.

TABLE 3 Absorbance Ratios from Latex-Modified Asphalt Concrete Mixes Obtained by Two Researchers

Asphalt-Aggregate Mix	No polymer	UP 2897 Modified Asphalt	UP 70 Modified Asphalt
Coastal + 1/2" gravel	0.0357 ± 0.0029 ^{a,b} 0.0395 ± 0.0021 ^b 0.0277 ± 0.0002 ^c	0.1649 ± 0.0100 ^b 0.1653 ± 0.0026 ^b 0.1690 ± 0.0000 ^c	0.1829 ± 0.0010 ^b 0.1886 ± 0.0056 ^b 0.1924 ± 0.0007 ^c
Ergon + 1/2" gravel	0.0041 ± 0.0041 ^b 0.0440 ± 0.0027 ^b 0.0341 ± 0.0001 ^c	0.1847 ± 0.0017 ^b 0.1871 ± 0.0025 ^b 0.1857 ± 0.0018 ^c	0.1891 ± 0.0004 ^b 0.2092 ± 0.0207 ^b 0.1959 ± 0.0018 ^c
Hunt + 1/2" gravel	0.0275 ± 0.0029 ^b 0.0291 ± 0.0033 ^b 0.0339 ± 0.0001 ^c	0.1711 ± 0.0024 ^b 0.1721 ± 0.0035 ^b 0.1829 ± 0.0030 ^c	0.1867 ± 0.0007 ^b 0.1758 ± 0.0025 ^b 0.1821 ± 0.0007 ^c
Coastal + dense graded gravel	NA ^d	0.1723 ± 0.0019 ^b 0.1733 ± 0.0028 ^b 0.1742 ± 0.0006 ^c	0.1836 ± 0.0028 ^b 0.1891 ± 0.0036 ^b 0.1870 ± 0.0009 ^c
Ergon + dense graded gravel	NA	0.1841 ± 0.0007 ^b 0.1890 ± 0.0039 ^b 0.1892 ± 0.0004 ^c	0.1966 ± 0.0034 ^b 0.1939 ± 0.0023 ^b 0.2007 ± 0.0007 ^c
Hunt + dense graded gravel	NA	0.1925 ± 0.0051 ^b 0.1876 ± 0.0018 ^b 0.1913 ± 0.0011 ^c	0.1802 ± 0.0052 ^b 0.1815 ± 0.0006 ^b 0.1870 ± 0.0005 ^c

^a Standard deviation of three FTIR scans on the same salt plate

^b Performed by researcher 1.

^c Performed by researcher 2.

^d NA = not available.

Analysis of EVA- and SBS-Modified Asphalt

The analysis procedure developed for SBR latex in asphalt cement was applied to samples of 2, 3, and 4 weight-percent EVA polymer in asphalt cement. The same three asphalts used in the analysis with SBR latex were used in this analysis. The EVA samples yielded two

peaks that were unique, both of which were attributable to acetate: 1242 cm^{-1} , which corresponds to C-O-C, and 1736 cm^{-1} , which corresponds to C=O. The ratio of the height of each of these peaks to the asphalt peak at 1375 cm^{-1} was determined. Ratios from both peaks are presented in Figure 4. The EVA in all three asphalt cements yielded R^2 values of 0.99. These analyses showed that the EVA polymer is readily quantified at these concentrations in three different asphalts.

Analysis of SBS in asphalt cement had one unique peak that was suitable for analysis. This peak appears at 966 cm^{-1} and is characteristic of the bending of the =C-H bond in the environment of the diene. The ratio of the 966- cm^{-1} peak against the 1375- cm^{-1} asphalt peak was determined. The data from the Exxon SBS in the three

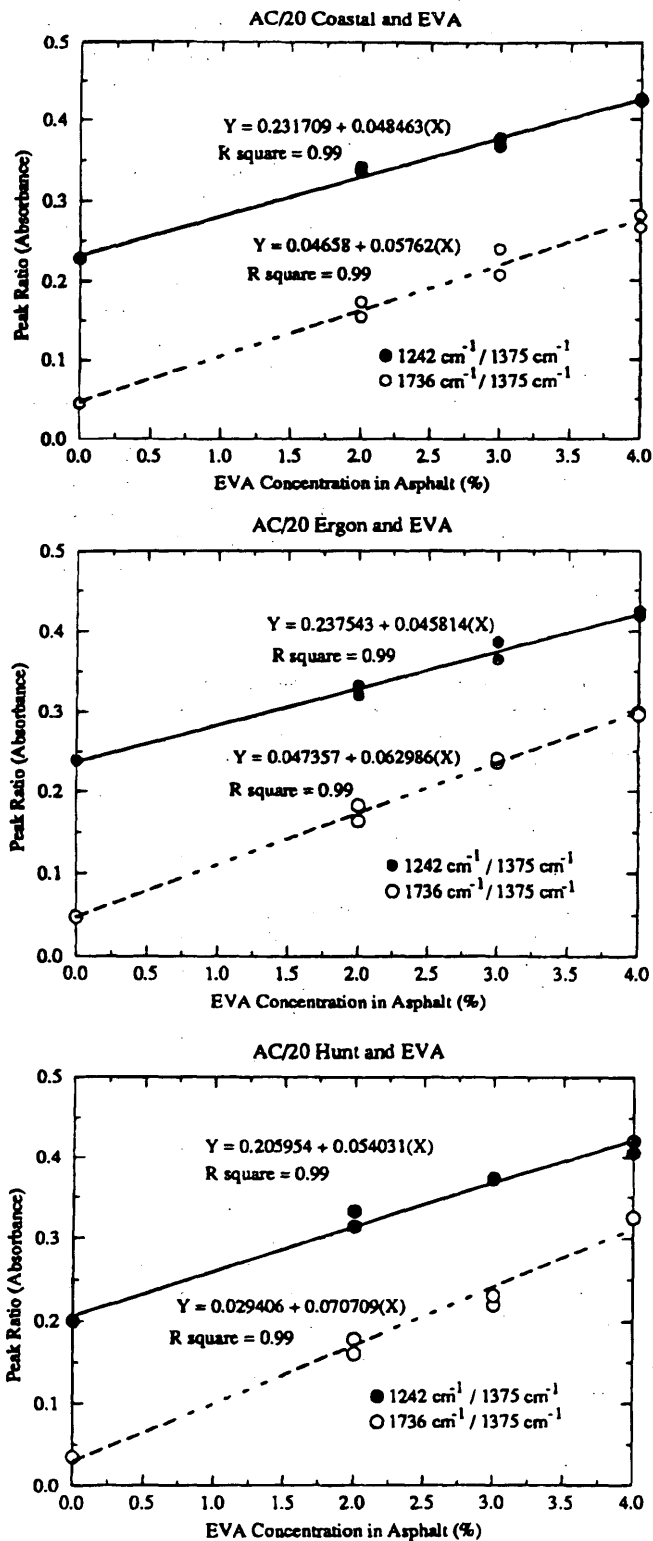


FIGURE 4 Calibration curves of EVA in asphalt.

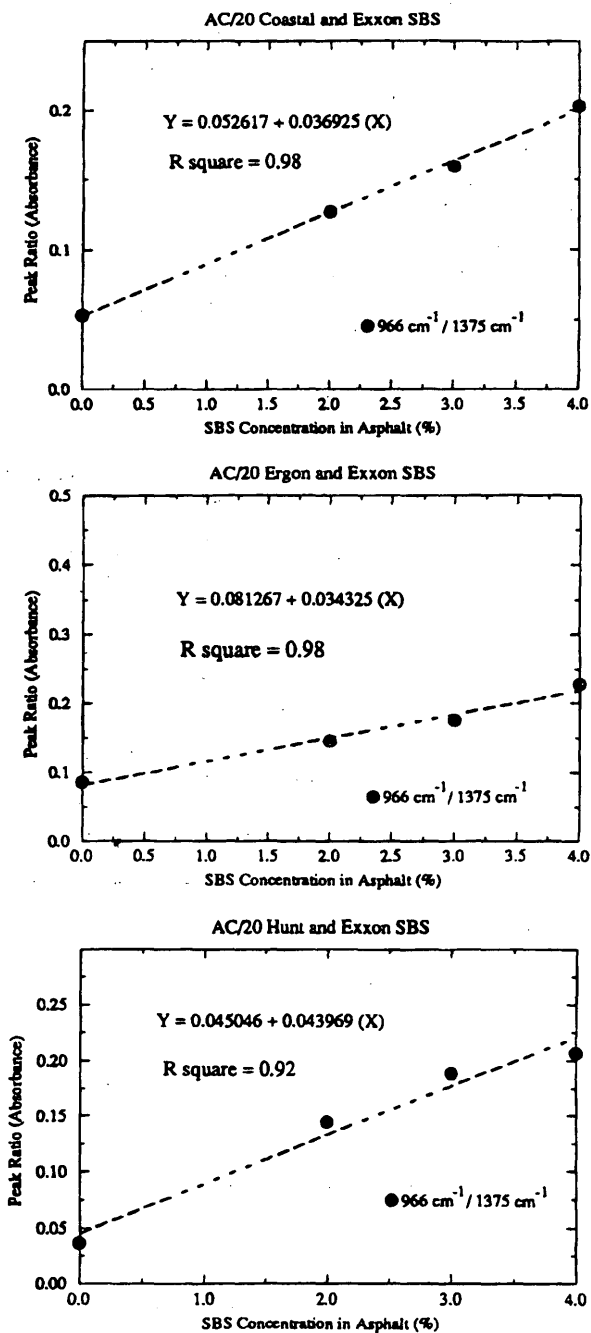


FIGURE 5 Calibration curve of SBS in asphalt.

asphalts are presented in Figure 5. The SBS in Coastal asphalt and Ergon asphalt yielded R^2 values of 0.98, whereas SBS in Hunt asphalt gave an R^2 value of 0.92. Figure 6 presents the data for SBS from Koch. The R^2 values obtained from Koch SBS were 0.98 for Coastal, Ergon, and Hunt asphalts; these values were slightly higher than those from Exxon SBS.

SUMMARY AND CONCLUSION

An analytical method that uses FTIR spectroscopy was developed for the analysis of two SBR latexes and EVA and SBS polymers in

asphalt cement. The method is reproducible and readily applicable to different latexes and asphalts. Calibration of EVA and SBS of 2 to 4 weight-percent polymer in asphalt was also achieved. Calibration curves of the SBR latex, EVA, and SBS materials in asphalt yielded R^2 values that ranged from 0.92 to 0.99. Application of the analysis to determine the actual concentration of latex in asphalt cement samples helped to explain the results from dynamic shear measurements. Successful analysis of 3 weight-percent SBR latex in asphalt samples was accomplished by removing the latex-modified asphalt with THF and analyzing the SBR latex content by the analysis procedure that was developed.

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REFERENCES

- Hoban, T. Modified Bitumen Binders for Surface Dressing. In *Chemistry and Industry*, Society of Chemical Industry, London, England, Sept. 3, 1990, pp. 538-542.
- Lenoble, C. Performance/Microstructure Relationship of Blends of Asphalts with Two Incompatible Polymers. *Fuel Science Technology International*, Vol. 10, No. 4-6, 1992, pp. 549-564.
- Paukkau, A. V. A. Ovchinnikov, R. K. Zacheslavskaya, E. R. Tsyrukun, and C. Y. Rappoport. Use of a Modified Morphological-Analysis System in Studies of Polymer-Asphalt Materials. *Stroitel'nye Materialov*, Ministerstvo Promyshlennosti, Moscow, Russia, 1990, pp. 21-22.
- Loucks, D. A., and F. P. Sequin. Determination of Low-Gel Polymer Content in Polymer-Modified Asphalt. U.S. Patent 4990456A, Feb. 5, 1991.
- Petersen, J. C., H. Plancher, and S. M. Dorrence. Identification of Chemical Types in Asphalts Strongly Adsorbed at the Asphalt-Aggregate Interface and Their Relative Displacement by Water. *Proc. Association of Asphalt Pavement Technologists*, Vol. 46, 1977.
- Petersen, J. C. Quantitative Functional Group Analysis of Asphalts Using Differential Infrared Spectrometry and Selective Chemical Reactions—Theory and Application. In *Transportation Research Record 1096*, TRB, National Research Council, Washington, D.C., 1986.
- Koenig, J. L. Spectroscopic Characterization of Polymers. *Analytical Chemistry*, Vol. 59, 1987, p. 1142.
- Painter, P. C., M. M. Coleman, and J. L. Koenig. *The Theory of Vibrational Spectroscopy and Its Application to Polymeric Materials*, John Wiley and Sons, Inc., New York, 1982.
- Choquet, F. S., and E. J. Ista. *Polymer Modified Asphalt Binders*. ASTM STP 1108 (K. R. Wardlaw and S. Shules, eds.), American Society for Testing and Materials, Philadelphia, 1991.
- Romine, R. A. The Determination of SBR-Latex Concentration in Asphalt Cements. Materials and Test Division, Texas State Department of Highways and Public Transportation, March 1987.
- Determination of Polymer Additive Percentages in Polymer Modified Asphalt Cements. Test Method TEX 533-C. Materials and Tests Division, Texas State Department of Highways and Public Transportation, March 1991.
- Test for Polymers in Asphalts. AHTD Test Method 432. Arkansas Highway Department.
- Lambert, J. B., H. F. Shurrell, L. Verbit, R. S. Cooks, and S. H. Stout. *Organic Structural Analysis*, MacMillan Publishing Co., Inc., New York, 1976, pp. 237-241.

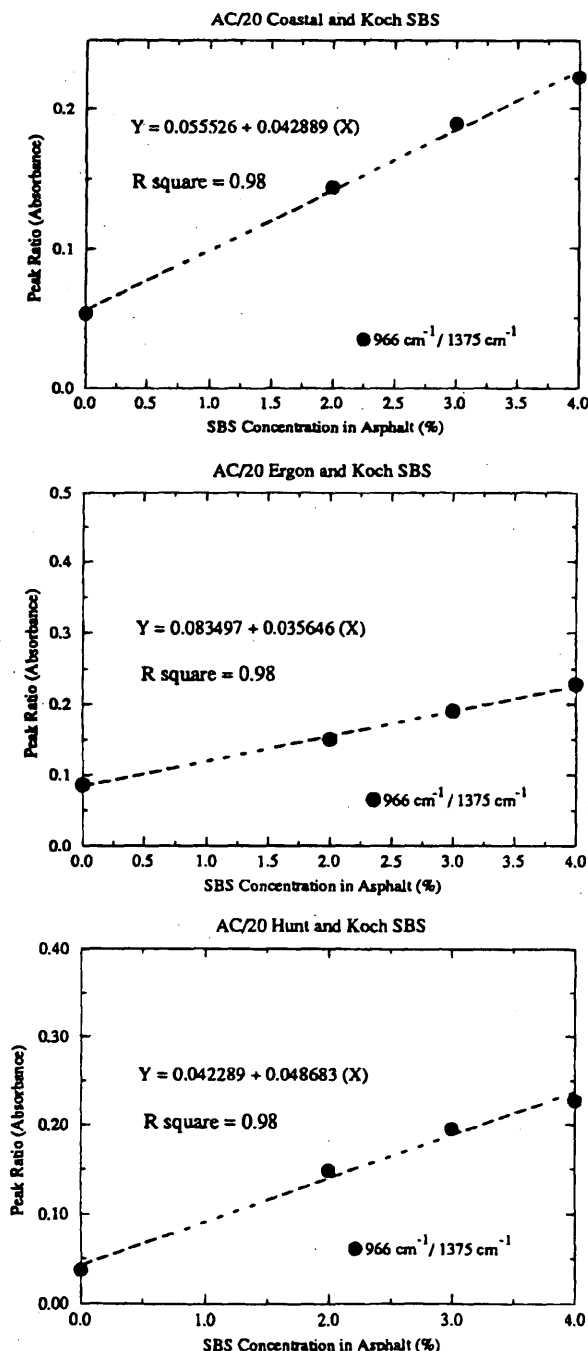


FIGURE 6 Calibration curve of Koch SBS in asphalt.