

Methods To Determine Polymer Content of Modified Asphalt

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A laboratory procedure using a Fourier transform infrared (FTIR) analyzer to quantitatively determine the polyethylene content of modified hot-mixed asphalt concrete paving mixtures was developed. FTIR provides a reasonably accurate and precise method for measuring polymer content of modified mixtures and is suitable for quality assurance testing for highway and airport agencies. However, certain factors limit the accuracy of the test, which is of concern when highly precise quantitative determinations are required. An attempt as made to develop a gravimetric procedure for quantitative analysis of polymer in asphalt paving mixtures. Although no successful procedure was generated, the findings were important because they revealed that the solubility of polyethylene is altered upon high-shear blending and exposure to hot asphalt cement.

Federal, state, and municipal highway and airport agencies purchase and apply paving materials using a variety of specifications and test procedures. To satisfy governmental regulations, the agency often must be able to accurately determine not only quality of materials but also content of certain components. In fact, certain highway agencies have expressed the desire for a test to accurately determine the polyethylene content of Novophalt in order to verify that their specifications are being met. Novophalt America, Inc., responded to this need by initiating a study at the Texas Transportation Institute at Texas A&M University to develop a test procedure to quantitatively measure the polyethylene content of modified binders and/or paving mixtures. The results of this work are applicable to any polymer-modified asphalt binder.

The primary objective of this research was to develop a test procedure using the Fourier transform infrared (FTIR) analyzer to quantitatively determine polyethylene (PE) content in Novophalt and paving mixtures containing Novophalt. A secondary objective was to investigate the merits of a gravimetric procedure using selected solvents to determine polyethylene content in Novophalt and paving mixtures containing Novophalt.

FTIR spectroscopy is routinely used to aid in analysis of binary compatible polymer blend systems. FTIR is used to qualitatively identify the presence of chemical functional groups. By measuring relationships between absorbance intensity and concentration and preparing calibration curves using known concentrations of materials of interest, accurate quantitative analyses can also be accomplished using FTIR. A procedure was developed to extract polyethylene-modified asphalt binder (Novophalt) from asphalt-aggregate mixtures, prepare cali-

bration curves, and measure polyethylene content of asphalt cement.

A gravimetric method to physically separate polyethylene from asphalt cement using selected solvents was evaluated. Although polyethylene is normally insoluble in the selected solvent, the polyethylene was finely divided and exposed to asphalt in the presence of heat (i.e., the Novophalt process), becoming mostly soluble. This work was preliminary and further effort is needed to fully understand the findings.

DESCRIPTION OF MATERIALS

The materials used in this study include asphalt cement, recycled polyethylene (mostly), aggregates, hot-mixed asphalt concrete, and organic solvents.

Asphalt Cement

The AC-10 asphalt used in this study was supplied by West Houston Asphalt in Houston, Texas. This asphalt was used in reconstruction of runways at Hobby Airport in Houston in fall 1988.

Polymer

A recycled polymer consisting mostly of polyethylene was used in this study. The same polyethylene had been used in the latter part of the runway reconstruction project at Hobby Airport. The polyethylene was produced by Bamberger Polymers, Inc., and contained some ethylene-vinyl acetate and carbon black as follows:

- Vinyl acetate, 3.0 percent,
- Carbon black, 2.5 percent,
- Density, 0.92 g/cc, and
- Melt index, 1.0 g/10 min.

Aggregates

Three aggregates were used in the various segments of the study. Washed coarse sand and washed river gravel were obtained from Gifford-Hill near College Station, Texas. These are siliceous, subrounded, nonporous materials used locally in construction of asphalt concrete pavement.

Crushed limestone was obtained from a White's Mines quarry near Brownwood, Texas. This material is characterized as a

very hard, low-porosity, low-absorption, and somewhat dolomitic limestone.

Gradation-specific gravity of the river gravel and limestone used in this study were approximately the same. Therefore, surface area per unit weight should be approximately equivalent.

Hot-Mixed Asphalt Concrete

Hot-mixed asphalt concrete was prepared in the laboratory, using the asphalt and aggregates described, to simulate paving mixtures. The aggregate was dried to constant weight in an oven at 325°F. The hot aggregate was mixed with hot Novophalt. The ratios of components in the mixture were as follows:

- Sand, 3000 g; Novophalt, 180 g; binder content, 5.66 percent
- River gravel, 1000 g; Novophalt, 53 g; binder content, 5.03 percent
- Limestone, 1000 g; Novophalt, 53 g; binder content, 5.03 percent.

Solvents

Solvents included trichloroethylene and methylene chloride, which have relatively low boiling points, and toluene and xylene, which have comparatively high boiling points.

FTIR METHOD

FTIR Equipment

The FTIR analyzer used in this investigation was a Nicolet Model 60 SX single-beam spectrometer. Specular reflectance was adapted as an accessory in the analysis of undiluted, opaque asphalt cement and polymer-modified asphalt. Infrared spectra with a bandwidth of 400 to 4000 cm^{-1} and 32 scans at a resolution of 4 cm^{-1} were signal-averaged and stored on a magnetic disk system.

Development of Calibration Curve

Sample Preparation

To simulate a binder extracted from a paving mixture, a sample of the pelletized black recycled polyethylene of known weight was dissolved in 20 ml of trichloroethylene at $70 \pm 5^\circ\text{C}$ using a reflux condenser and stirred for 30 min. To identical solutions, samples of hot asphalt of different weights were added and stirred for 2 hr at 70°C until the blend became a homogeneous system. Specimens were removed from this solution and placed on specially prepared aluminum plates, and the trichloroethylene was removed by evaporation under vacuum at room temperature.

Calibration Curve

Using this procedure, 10 different blends of the polymer in asphalt were prepared. The dosages of polymer in asphalt included 1.6, 1.8, 3.0, 4.6, 5.1, 6.4, 7.1, 8.1, and 9.9. Selected vertical peak heights on the FTIR absorbance plot were measured manually from the baseline. The most informative bands for these particular materials were between 1755 and 1530 cm^{-1} for asphalt and between 1820 and 1725 cm^{-1} for the polymer. The ratio of the peak heights representing absorbance at two distinct wavelengths was used to construct the calibration curve. For routine testing, approximately four points should produce a satisfactory calibration curve.

The infrared spectra for the asphalt used in this study show distinct, relatively interference-free absorption band peaks at frequencies of 1601, 1461, and 1376 cm^{-1} in the 400- to 2000- cm^{-1} region with a high degree of reproducibility (Figure 1). For this particular polymer, peaks occur at 1738, 1462, and 1376 cm^{-1} (Figure 1). The peaks at 1460 and 1376 cm^{-1} are common to both the polymer and the asphalt and therefore cannot be used as an accurate measure of polymer content in this particular Novophalt product. The small peak at 1738 cm^{-1} in the spectra of the polymer is attributed to the carbonyl functional group in the polyvinyl acetate. The peak at 1601 cm^{-1} for the asphalt is attributed to double bonds in benzene rings (aromatic hydrocarbons).

These unique frequencies at 1601 and 1738 cm^{-1} were chosen for determining the relative concentration of polymer in asphalt using infrared spectroscopy (Figure 2). Ratios of these two absorbance frequencies for asphalt-polymer blends of several known concentrations were determined and plotted (Figure 3). Theoretical considerations for these measurements of absorbance and computations of ratios are given in a subsequent section of this report. Standard linear regression techniques were applied to construct the calibration curve. Polyethylene content was not determined directly; rather, concentration of a component of the polymer, vinyl acetate, was measured. The assumptions were made that polymer components were completely homogeneous and that the extraction process did not preferentially separate out any of the polymer components.

Reference Spectra

In this research, a technique was developed to facilitate FTIR testing of undiluted asphalt. The asphalt samples were mounted on specially designed aluminum plates for FTIR testing. The aluminum plates were chemically treated to remove the oxidized layer and polished to provide an extremely smooth surface. After the instrument and sample compartment of the FTIR was purged with nitrogen for at least 15 min, a blank aluminum plate was placed in the compartment and reference spectra were obtained. FTIR spectra were then obtained for aluminum plates coated with the asphalt blends. The FTIR spectra of the modified asphalts were obtained by subtracting the reference spectra of the blank plate from those of the binder-coated plates. The FTIR analyzer is designed to perform this function automatically.

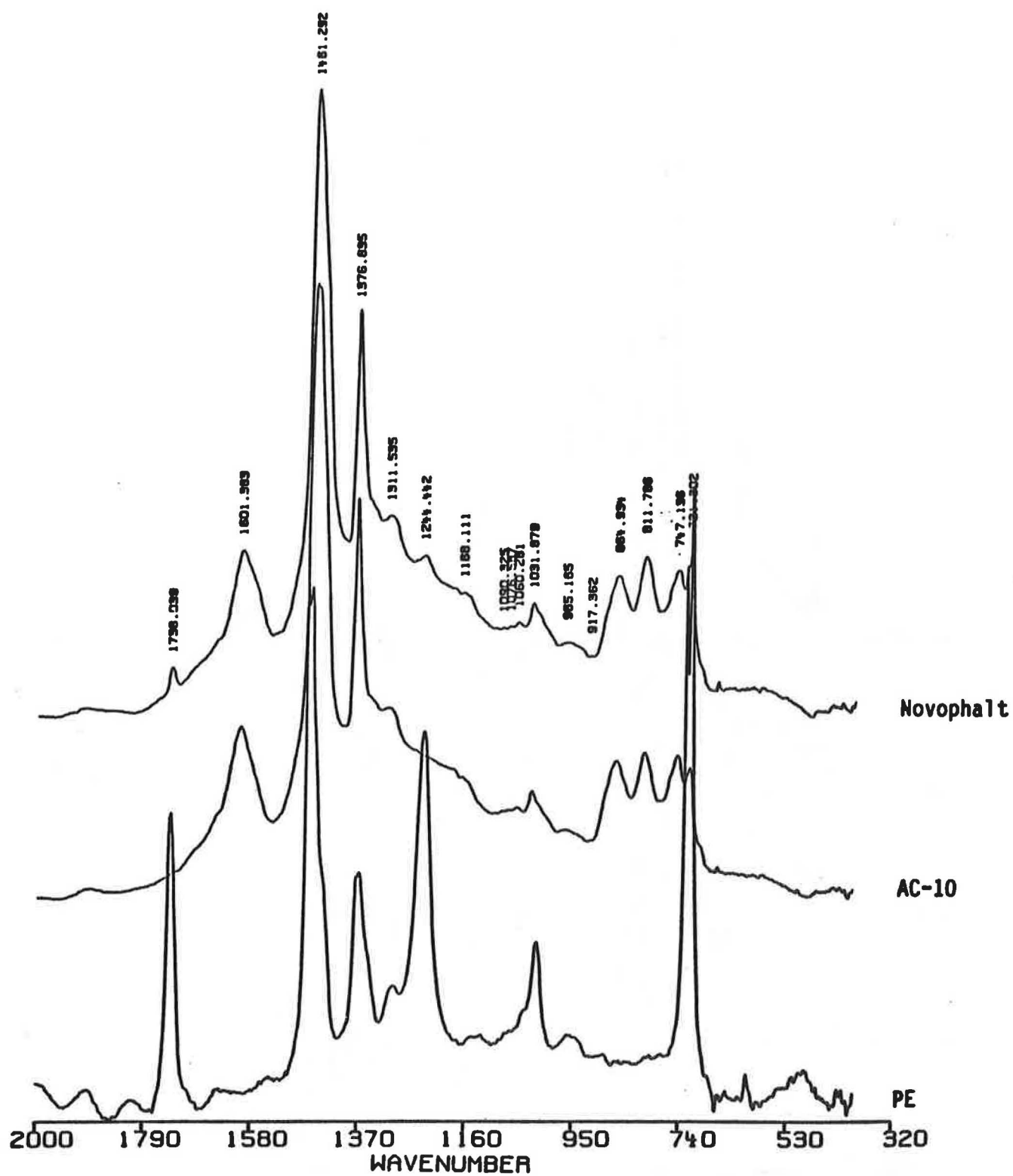


FIGURE 1 Infrared spectra (2000 to 400 cm⁻¹) for Novophalt, asphalt, and polyethylene (black).

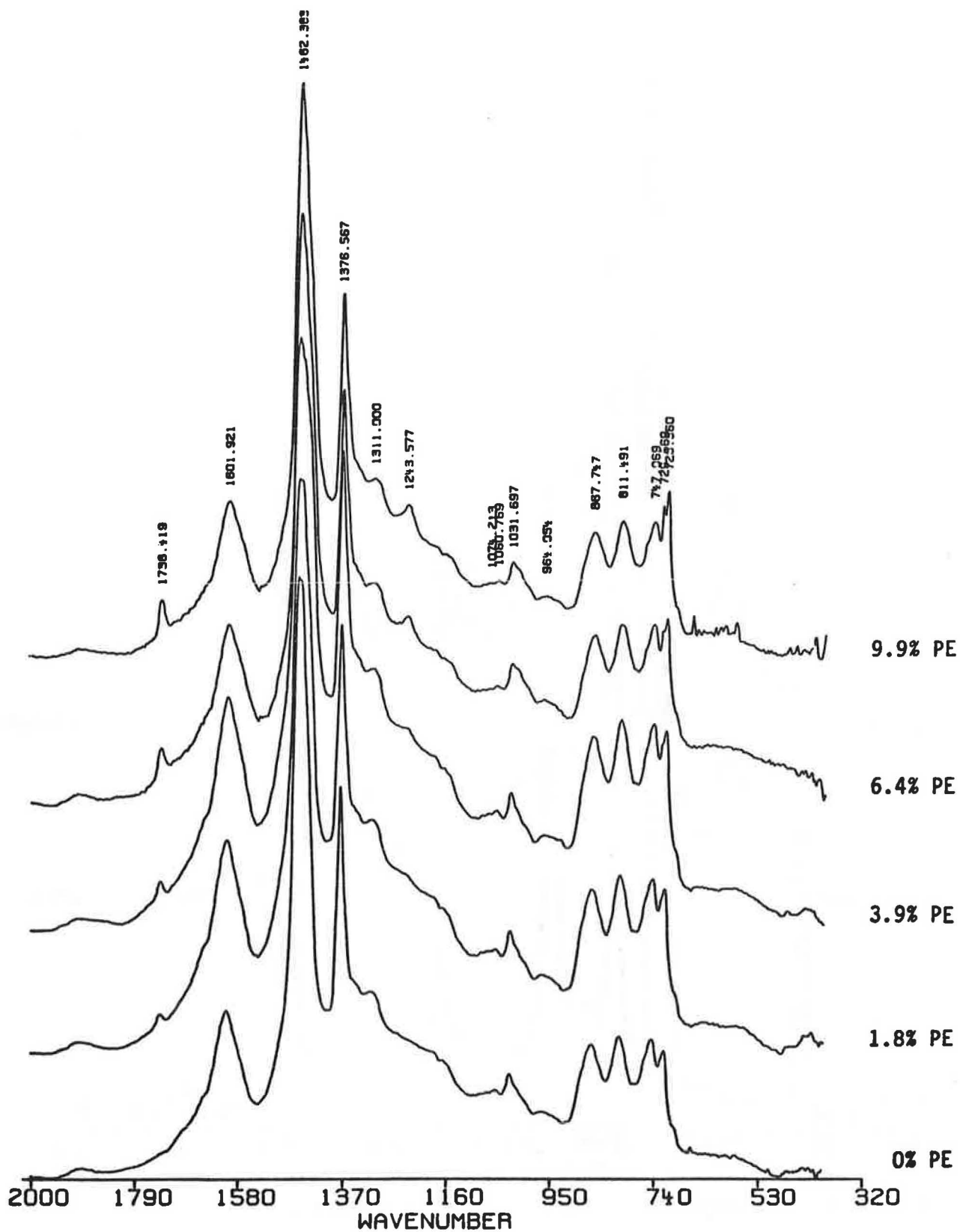


FIGURE 2 Infrared spectra (2000 to 400 cm⁻¹) for different polyethylene contents in asphalt.

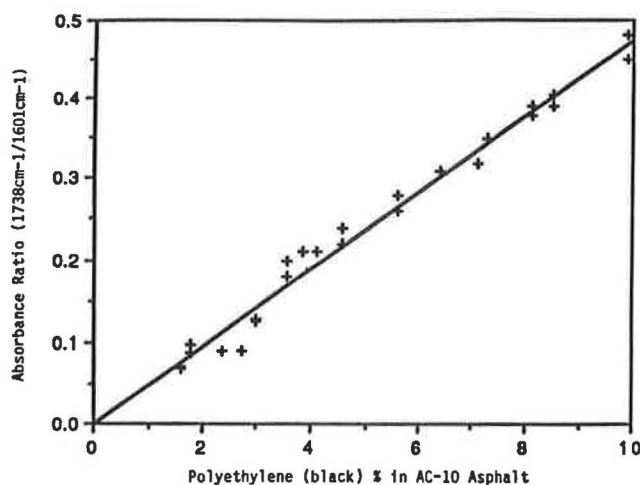


FIGURE 3 Calibration curve for polyethylene (black) content in AC-10 asphalt for —C=O/—C=C— functional group absorbance ratio.

Verification

To verify the utility of the calibration curve, a sample of the polymer was accurately weighed, dissolved in xylene, and mixed with an accurately weighed sample of asphalt. After evaporation of the solvent, the FTIR analyzer measured the polymer content of the asphalt. The known polymer content was 4.72 percent; the FTIR measured 4.69 percent. Therefore, the difference was 0.03 percentage points. Eight measurements were made to obtain the mean, which yielded a standard deviation of 0.083 percent and a coefficient of variation of 1.8 percent. These data indicate that the method is both accurate and precise.

Precautions

FTIR spectra are unique for a particular polyethylene and asphalt; therefore, a new calibration curve must be developed each time new materials are used to produce Novophalt.

The FTIR calibration curve would normally be developed using neat asphalt and polymer. If samples for subsequent analysis are taken from a paving mixture prepared using Novophalt in an asphalt mix plant, significant changes may have occurred in the polymer and asphalt. During the production of Novophalt, chain scission in the polymer can occur. Hot storage of this material may cause certain unknown chemical reactions between the two substances. During plant mixing, both the asphalt and the polymer undergo oxidation, which changes the functionality of both products. Other unknown chemical reactions may occur in the solvent extraction process. These chemical reactions can significantly affect the spectra obtained on the FTIR and thus reduce the accuracy of the quantitative analysis.

Sample Testing

Methodology

Quantitative measurement of polymer in asphalt using FTIR must be preceded by the development of a calibration curve

using known concentrations of the materials in question, as discussed earlier. To quantitatively determine the percentage of polyethylene in the modified binder of a sample of asphalt-aggregate mixture, the modified binder must first be extracted from the mixture. Then FTIR spectra are obtained using the aluminum plate method, and the ratios of the peak heights representing absorbance at the appropriate wavelengths are compared with the calibration curve to directly interpolate the polyethylene content.

A reflux extraction process is probably the best method to separate Novophalt and aggregate. This process minimizes the quantity of solvent required. Suitable solvents to extract asphalt and ensure that the polyethylene is also extracted include high boiling point solvents such as xylene (boiling point, 140°C), perchloroethylene (121°C), or toluene (111°C). Toxicity and flash point of the solvents should also be considered. The optimum time period to carry out the reflux process depends on the solvent selected but may be several hours. This limited study did not permit an evaluation of solvent effectiveness or optimization of the extraction time period. Only xylene was examined in this portion of the work. Reflux extraction was allowed to proceed until the filtrate became a light straw color.

Test Results

Asphalt-aggregate mixtures were prepared in the laboratory. An extraction process using xylene at 140°C was used to separate Novophalt from three different aggregates (Table 1). About 8 hr were required to reach the end point (light straw color of filtrate), depending on the type of aggregate. More time was required for the limestone (8 hr), as compared to the coarse sand and river gravel (6 hr).

On the average, about the same proportion of binder was extracted from each of the different aggregates, using the reflux-xylene process. However, based on results of FTIR testing, significantly less polymer was present in the binder extracted from the limestone when compared with that extracted from the siliceous aggregates (Table 1). Slightly less polymer was present in the extract from the sand compared with that from the river gravel. These limited data indicate that the efficiency of extraction of polyethylene depends on aggregate composition, absorbancy, and grain size. Polyethylene may be more strongly adsorbed on calcareous aggregates than on siliceous aggregates. Polyethylene adsorption increases as surface area per unit weight of aggregate increases.

FTIR analysis is an accurate method for determining polymer content of modified asphalt binder. FTIR analysis provides exceptionally good repeatability. The disadvantage of routinely testing a large number of different mixtures is the length of time (20 to 24 hr) required to prepare the calibration curve.

Theoretical Derivation and Practical Application

Quantitative infrared analysis is based on Beer's law. Apparent deviations arise from either chemical or instrumental effects. Low absorbance values were used to minimize the presence of scattered radiation, which makes the direct application of Beer's law inaccurate.

TABLE 1 RESULTS OF EXTRACTION OF ASPHALT MIXTURE WITH XYLENE AND ANALYSIS OF POLYETHYLENE CONTENT OF EXTRACTED BINDER USING FTIR

Test No.	Mix Weight, grams	Aggregate in Mix Type	Weight, percent of mix*	Novophalt In Mix, percent of mix*	PE in Novophalt**, percent of mix*	Novophalt Extracted, percent of mix*	PE in Extracted Novophalt, percent of binder*	From FTIR Weight Change, percent of mix*
1	55.696	Sand	94.34	5.66	5	5.08	4.9	-0.12
2	56.107	Sand	94.34	5.66	5	5.52	4.9	-0.02
3	68.569	Gravel	94.97	5.03	5	4.91	5.1	-0.12
4	71.259	Gravel	94.97	5.03	5	4.86	5.0	0.05
5	57.275	Limestone	94.97	5.03	5	4.86	4.1	-0.51
6	58.612	Limestone	94.97	5.03	5	4.80	4.1	-0.55
7	61.203	Limestone	94.97	5.03	5	4.78	4.2	-0.36
8	64.427	Limestone	94.97	5.03	5	4.67	4.2	-0.35
9	46.646	Sand	94.94	5.66	5	5.32	4.8	+0.02
10	54.094	Sand	94.34	5.66	5	5.49	4.9	-0.04
11	54.505	Sand	94.34	5.66	5	5.62	4.9	-0.14
12	60.484	Sand	94.34	5.66	5	5.59	4.9	-0.07
27	61.426	Sand	94.34	5.66	5	5.43	5.0	-0.07
28	68.936	Gravel	94.97	5.03	5	5.50	5.0	-0.12
30	61.554	Limestone	94.97	5.03	5	4.48	4.1	-0.22

* Indicates percent by weight.

** Novophalt was prepared in Houston, Texas and the value of PE content is approximate.

$$A = alC \quad (1)$$

where

A = absorbance of compound,
 a = absorptivity of compound,
 l = sample path length (film thickness), and
 C = concentration in weight percent of compound.

In the analyses it is imperative, for practical reasons, to use the values for ratios rather than absolute absorbance values. If the absorbance of polyethylene copolymer at 1738 cm^{-1} is defined as $A_{[PE]}$ and the absorbance of asphalt at 1601 cm^{-1} is defined as $A_{[AC]}$ the ratio of the two absorbance values becomes

$$R = A_{[PE]}/A_{[AC]} \quad (2)$$

The concentration (weight percent) of polyethylene and asphalt in a sample of Novophalt is defined as C_{PE} and C_{AC} , respectively, to correspond with the above definitions. According to Beer's law, the absorbance values are related to the concentrations in the following manner:

$$A_{[PE]} = alC_{PE} \quad (3)$$

and

$$A_{[AC]} = blC_{AC} \quad (4)$$

where a and b equal absorptivities of polymer and asphalt, respectively. Dividing Equation 4 into Equation 3 yields

$$\frac{A_{[PE]}}{A_{[AC]}} = \frac{aC_{PE}}{bC_{AC}} \quad (5)$$

If a and b are assumed to be constants, the ratio of a/b must be a constant as well. Let us define

$$K = \frac{a}{b} \quad (6)$$

and the reciprocal

$$K' = \frac{1}{K} = \frac{b}{a} \quad (7)$$

Then

$$R = K \frac{C_{PE}}{C_{AC}} \quad (8)$$

and

$$\frac{C_{PE}}{C_{AC}} = K'R \quad (9)$$

It follows that the ratio of absorbance (R) is directly proportional to the ratio of concentrations of the components. The plot in Figure 3 demonstrates a very good linear relationship between R (abscissa) and the ratio C_{PE}/C_{AC} (ordinate).

This relationship (Figure 3), which has previously been termed a "calibration curve," can be used to readily determine the proportion of polymer to asphalt in an unknown sample, given the ratio of absorbance (R).

The concentration of polymer could be calculated directly from the ratio of concentrations as demonstrated below:

$$C_{PE} = 100 \frac{C_{PE}/C_{AC}}{(1 + C_{PE}/C_{AC} - AC)} \quad (10)$$

where the C_{PE}/C_{AC} ratio is obtained by reading the graph based on the value of R . However, this approach is complicated. Direct reading from a graph of the polymer content is desirable.

In a two-component system, the concentration of one component can be expressed, by definition, in terms of the other:

$$C_{AC} = 100 - C_{PE} \quad (11)$$

Other ratios, such as 1460/1601 or 1376/1601, could have been used to construct a calibration curve, but the $-\text{CH}_2$ and $-\text{CH}_3$ functional groups were present in both polyethylene and asphalt. Therefore, infrared absorbance was not very sensitive to changes in the $-\text{CH}_2$ or $-\text{CH}_3$ functional groups with varying concentrations of polyethylene in asphalt. The relative content of the $-\text{CH}_3$ group in both polyethylene and asphalt is comparatively low and subject to change during processing. For these reasons, the ratios of 1376/1601 and 1460/1601 were not used in determining polyethylene content of Novophalt.

GRAVIMETRIC METHOD

Two-Step Extraction Procedure

A two-step extraction process was used for quantitative analysis of polyethylene content of Novophalt in hot-mixed asphalt concrete. This method is based on the fact that asphalt and polyethylene have different solubilities in certain solvents at different temperatures. In methylene chloride, asphalt is quite soluble but polyethylene is insoluble. Polyethylene is soluble in certain solvents with high boiling points, such as xylene or toluene at or near their boiling points.

To verify that the polyethylene used in this study is insoluble in methylene chloride, a sample of polyethylene was placed in the soxhlet extractor and allowed to reflux for 24 hr. There was no visible change in the polyethylene. The carbon black in the polyethylene did not cause even the slightest discoloration of the filter.

In Step 1, a sample of Novophalt-aggregate mixture weighing 60 to 70 g was placed in the thimble of a soxhlet extractor and the binder was extracted using methylene chloride at 40°C. This step was stopped when the filtrate became a light straw color, after approximately 4 hr. Step 1 should have

removed only the asphalt, leaving the polyethylene with the aggregate. The mass of extract and the material retained in the thimble were dried and weighed separately.

In Step 2, the retained material was again extracted using the soxhlet extractor with xylene at 140°C for approximately 48 hr. This extended extraction time is probably not required but was used to ensure that all soluble material (ideally polyethylene) was removed from the aggregate. The mass of extract and the aggregate retained in the thimble were dried and weighed. Weights of the dry materials were used to calculate binder content of the mix and any weight changes that may have occurred (Table 2). The material extracted in Step 2 appeared to be mostly polyethylene, but an FTIR analysis was not performed because the calibration curve was valid for a maximum polyethylene concentration of 10 percent.

Although considerable care was exercised, unaccountable weight losses occurred. Vacuum distillation of the solvents may have removed some of the lighter hydrocarbons in the asphalt. Certain components in the asphalt may have formed azeotropes with the solvents and evaporated during drying. The limestone mixtures experienced the greatest weight losses by far. This may be explained by decomposition of selected aggregate components (such as hydrates) upon exposure to the high temperatures.

FTIR Analysis of Extract

The extract from Step 1 was analyzed to determine the polyethylene content (Figure 4) using FTIR and the procedures described previously. The result revealed that a significant portion of the polyethylene was extracted by the methylene chloride. This important finding indicates that the nature of the polyethylene was changed significantly during production of Novophalt so that it became partially soluble in methylene chloride. These changes most likely occurred during the high-shear blending process, heating, mixing with aggregate, and storage. Chain scission of the polyethylene may have occurred, which reduced the molecular size and changed the solubility parameters. This is a good reason for not using absorbance bands associated with CH_2 and CH_3 groups. In addition, the oils and resins in the asphalt and the heat likely

TABLE 2 RESULTS OF TWO-STEP GRAVIMETRIC ANALYSIS OF NOVOPHALT USING METHYLENE CHLORIDE AND XYLENE

Test No.	Mix Weight, grams	Aggregate Type	Initial Condition		Step 1		Step 2		Weight Change Of Mix, percent of mix
			Aggregate Weight, percent of mix	Novophalt* In Mix, percent of mix	Binder Extracted From Mix, percent of mix	PE In Extracted Binder,** percent of binder	Binder Extracted From Aggr, percent of mix	Aggregate Remaining, percent of mix	
13	63.699	Sand	94.34	5.66	5.35	5.1	0.17	94.49	+0.01
14	60.546	Sand	94.34	5.66	5.30	5.2	0.11	94.60	+0.01
15	65.803	Sand	94.34	5.66	5.24	4.8	0.24	94.48	-0.04
16	63.388	Sand	94.34	5.66	5.21	4.8	0.08	94.65	-0.06
17	59.184	Sand	94.34	5.66	5.25	4.8	0.16	94.51	-0.08
18	62.611	Sand	94.34	5.66	5.24	4.8	0.20	94.44	-0.12
23	66.061	Gravel	94.97	5.03	4.82	4.3	0.07	94.95	-0.16
25	61.515	Gravel	94.97	5.03	4.90	4.4	0.06	95.00	-0.04
24	60.169	Limestone	94.97	5.03	4.90	3.7	0.08	94.71	-0.39
26	61.337	Limestone	94.97	5.03	4.82	3.6	0.09	94.97	-0.21

* Novophalt was prepared in Houston, Texas and contains approximately 5 percent polyethylene (PE).

** PE content measured using FTIR.

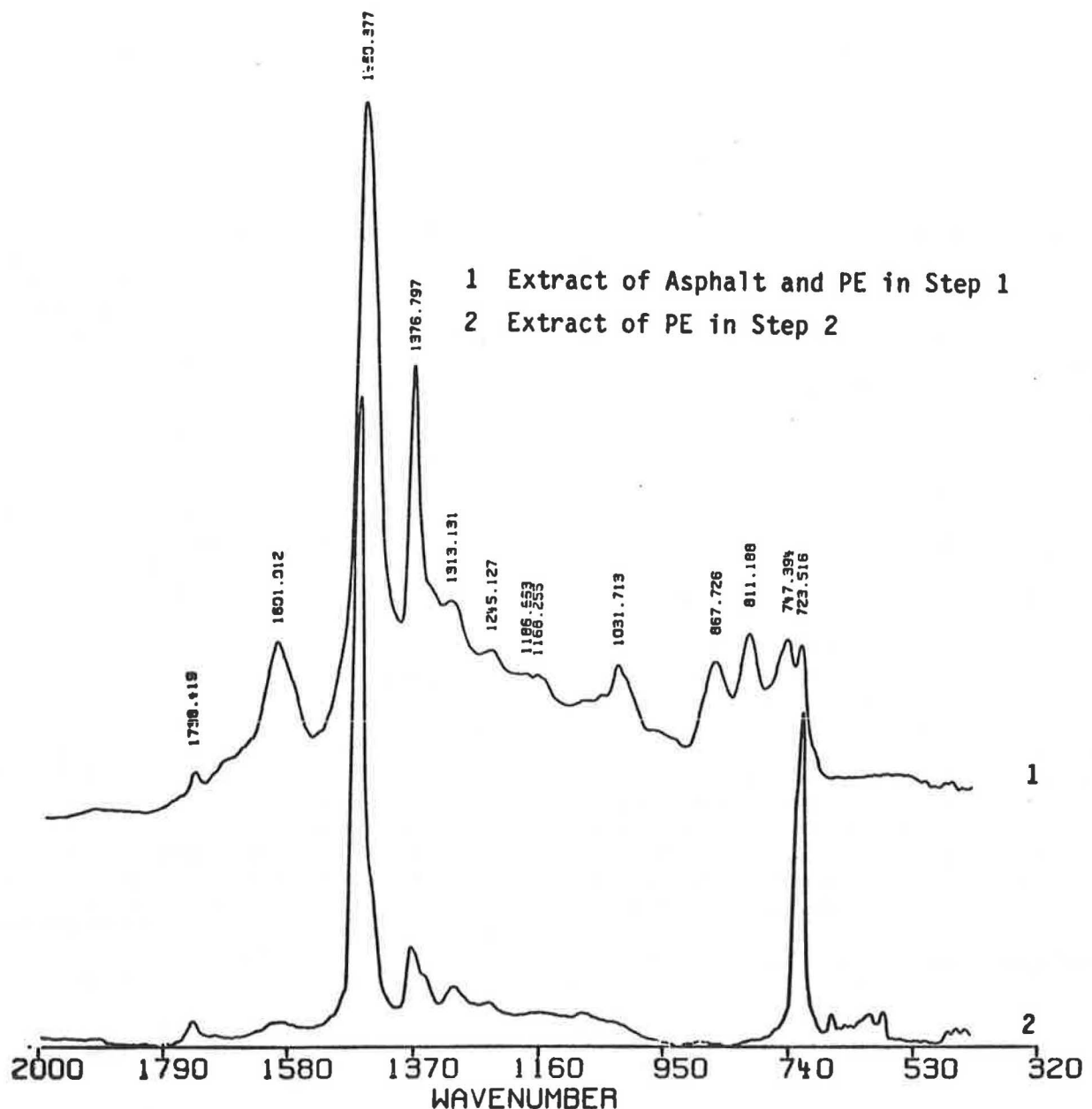


FIGURE 4 FTIR analysis of extracts from Steps 1 and 2 of gravimetric procedure.

caused the polyethylene particles to soften and swell, which further altered the solubility.

Effect of Aggregate Type on Polyethylene Extraction

By using either methylene chloride or xylene as a solvent, more polyethylene was retained by the limestone than by the river gravel or the sand (Table 3). This finding indicates that the polyethylene is more strongly adsorbed on the limestone aggregate than on the siliceous materials. Gradations and thus surface areas per unit weight of the two coarse aggregates were approximately the same. Water absorption tests on ag-

gregates of similar gradation from these two sources has shown only slightly greater absorption for the limestone. The sand and river gravel were obtained from the same source, thus chemical composition of the two should be similar. Therefore, this phenomenon appears to be related to the chemical properties of the aggregates.

CONCLUSIONS

1. FTIR is a reasonably accurate and precise procedure for measuring polymer content of modified asphalt binder. The

TABLE 3 EXTENT OF EXTRACTION OF
POLYETHYLENE FROM DIFFERENT AGGREGATES
USING DIFFERENT SOLVENTS

Aggregate Type	Solvent	Extraction time, hour	PE in Extracted Binder,* percent	Approximate Quantity of PE Extracted by Solvent, percent
Sand	MC**	4	4.8	96
Sand	MC	4	4.8	96
Sand	MC	4	4.0	80
Gravel	MC	4	4.3	86
Gravel	MC	4	4.4	88
Limestone	MC	4	3.6	72
Limestone	MC	4	3.7	74
Sand	Xylene	6	4.9	98
Sand	Xylene	6	4.9	98
Gravel	Xylene	6	5.1	102
Gravel	Xylene	6	5.0	100
Limestone	Xylene	6	4.1	82
Limestone	Xylene	6	4.1	82
Limestone	Xylene	8	4.2	84
Limestone	Xylene	8	4.2	84

* Measured Using FTIR

** Methylene Chloride

chief disadvantage of the procedure is the time required to prepare the calibration curve necessary for quantitative analysis using FTIR. Typically, at least 1 staff-day is required to prepare a suitable calibration curve.

2. Completeness of the extraction of polyethylene or asphalt from aggregate depends on the aggregate composition and gradation, solvent, temperature, and time.

3. Limited data indicate that polyethylene is more strongly adsorbed on limestone than on siliceous aggregates and, further, that polyethylene is more strongly adsorbed on fine-grained siliceous aggregate than on similar coarse-grained material.

4. A two-step gravimetric procedure using solvents to quantitatively determine the polyethylene content of Novophalt cannot be performed without first finding a solvent that will selectively dissolve asphalt and not affect the polyethylene as it exists in the Novophalt.

5. The solubility of polyethylene is altered when incorporated in asphalt to produce Novophalt. Polyethylene is not normally soluble in methylene chloride, but when exposed to the Novophalt production process and the aggregate mixing process, it becomes mostly soluble.