

Quantitative Analysis of Joint Sealants Using FTIR-ATR

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Fourier transform infrared spectroscopy using attenuated total internal reflection (FTIR-ATR) was found to be a reliable analytical method for evaluating a two-component joint sealant material. A calibration curve was developed from measuring the peak heights of infrared absorption bands unique to the different components in the two-component coal-tar modified polymeric joint sealant and relating these to the weight percent of the base component. A nonlinear relationship was found to exist between the ratio of the peak height of Component A over the peak height of Component B versus the weight percent of Component B added to the two-component mixture. FTIR-ATR proved to be a useful and expedient way to evaluate the composition of the joint sealant during or after the mixing and curing process; it may, after appropriate investigation, have potential for use in quality control of joint sealing material installations and forensic investigations of failures in such installations.

Many pavement engineers, contractors, and manufacturers have been less than satisfied with the field performance of some pavement joint sealant materials. Sealant materials that are supposed to perform satisfactorily for 10 years are failing in 1 to 3 years; some user agencies report failure within 6 months after installation (1,2). The reasons provided for the premature failure of the sealant often depend on who is providing the explanation. For the pavement engineer or user agency, the cause of failure is normally believed to be an inferior sealant material, poor workmanship, or both. The contractor will cite problems associated with the project specifications, the inspection procedures or requirements used by the user agency, or an inferior product supplied by the manufacturer. The manufacturer will cite project specifications or contractor deficiencies. Any one or all of these reasons could contribute to the unsatisfactory field performance of a pavement joint sealant on a specific project. Regardless of the cause of the failure, corrective action must be taken and lessons must be learned to prevent the failures from reoccurring.

The reason for finding solutions to the poor field performance of joint sealant materials is financial. The user agency specifies a joint sealant material to protect the pavement structure, thereby extending the life of the pavement and reducing the maintenance costs. When the sealant prematurely fails, not only has the protection to the pavement been lost, but the maintenance costs have increased because the sealant must be replaced. The financial loss to both the contractor and manufacturer may be more direct. They may be required to reseal the joints, increasing their labor and materials cost. Their reputations may have been damaged be-

cause of what was perceived as a poor job or inferior material. Such perceptions can cause the contractor to lose future projects and the manufacturer to lose sales.

More and more, user agencies, contractors, and manufacturers are trying to work together to provide a high-quality, long-lasting finished product. User agencies have incorporated manufacturers' information about joint preparation requirements and sealant application techniques into the project specifications, and materials testing by an independent laboratory is sometimes required. Inspectors learning the proper procedures for sealing projects and some contractors are striving to instill in all of their personnel that quality control is a high priority. Manufacturers are providing technical support to the contractor, answering questions such as "How clean is clean?" and specifying the environmental conditions under which their material can be successfully installed (i.e., temperature, humidity, etc).

The cooperation between these three groups should eventually help joint sealing projects, but this cooperation is not yet widespread—even when all phases of the project have been conducted well, failures still occur. For example, the personnel on one resealing project conducted at a military base stated that the sealant material was tested and conformed to the appropriate material specification, the joints were "hospital clean," and the sealant was installed properly, but the sealant failed within 3 years. Why did it fail? One can study the contract specifications and conduct field evaluations to determine the joint width, depth, spacing, sealant shape factor, and current sealant condition to speculate with some accuracy about possible causes for the failure. But forensic test methods are not available to determine if some type of contamination was introduced into the sealant to cause the failure. Current conventional joint sealant test methods cannot determine if a hot-applied sealant was overheated, if a two-component sealant was properly mixed, or if the sealant was damaged during shipping. One method that could be useful for such analysis is the Fourier transform infrared spectroscopy—attenuated total internal reflectance (FTIR-ATR).

BACKGROUND

Fourier transform infrared spectroscopy has become a very reliable analytical method for performing quality control of systems containing several different chemical constituents. An especially useful development has been the ATR technique. Using this technique, the sample to be analyzed is pressed against an internal reflectance element (IRE). An infrared beam of light is passed through the IRE, which causes the

beam to undergo multiple internal reflections. These internal reflections create an effect called the evanescent wave, which extends beyond the IRE-sample interface into the sample. The internal reflectance of infrared occurs in the IRE as long as the refractive index of the sample is less than that of the IRE it is touching. For wavelengths at which the sample exhibits absorption, this condition is lost; that is, the complex refractive index of the sample will exceed that of the IRE and light is lost. The spectrum obtained is that of light lost into the sample. This is important: the ATR spectrum represents a dispersive (refractive index) effect and is not based on absorptive processes described by Beer's law. The evanescent wave also decays exponentially as it passes into the sample, making the ATR measurements independent of sample thickness (Figure 1) (3).

Considerable work has been done using FTIR-ATR to study the composition and behavior of chemical systems. The research efforts vary from the study of the macromolecular orientation in the polymer surfaces of uniaxially drawn polypropylene sheets (4) to the reinforcement mechanism existing between silane coupling agents and glass (5). FTIR-ATR was also found to be an ideal method for quantitative analysis of complex mixtures used in carbon-epoxy composite materials. The FTIR-ATR technique has two advantages: spectra obtained using ATR have been shown to provide a more detailed spectrum than those obtained by transmission or reflectance modes for intractable samples (6), and samples can be tested in their processed state without time-consuming solvent extraction and film preparation. For pavement joint sealants, this means that it is possible to obtain meaningful analysis of samples obtained from the field. This is not true of conventional joint sealant tests.

The current study is using the FTIR-ATR sampling technique to evaluate joint sealant materials used for pavement sealing projects. The objective is to determine the feasibility of using FTIR-ATR as a quality-control test for measuring the mixing ratios of joint sealant materials after application in the field.

EXPERIMENTAL METHOD

Materials

The material used in this preliminary study was a two-component, cold-applied material manufactured to meet the

requirements of Federal Specification SS-S-200E, Type H, Amendment 1 (Table 1). This specification requires the sealant to be both fuel- and blast-resistant. Type H means the sealant is mixed and applied using hand tools instead of sealant application equipment. Originally, a Type M or machine-mixed sealant was to be used for the FTIR-ATR analysis because improper mixing of the Type M material is a common complaint from personnel involved with sealant projects. The Type M material could not be uniformly mixed in different ratios in the laboratory by hand; therefore, the Type H sealant was selected. If different mixing ratios can be determined with the Type H material, it is believed that the method can eventually be transferred to Type M sealants. A second sample of the two-component, cold-applied sealant was obtained for method verification. The second sample was the same product as the first but from a different lot.

Sample Preparation

The two-component, cold-applied sealants were mixed in various ratios by weight and then poured into a mold to produce a sample 2 mm thick, 25 mm wide, and 75 mm long. The weight ratios were determined by measuring each component and then pouring Component A (accelerator) into the container that contained Component B (base). The empty Component A container was reweighed to determine the exact mixing ratio. The mixing ratios are provided in Table 2. The first and last entries in Table 2 represent pure Component A and pure Component B, respectively, which were also analyzed using FTIR-ATR. After the two components were added together, they were mixed manually for approximately 10 min. The mixture was observed under a black light to ensure that it had been uniformly mixed. The samples were then poured into the molds and allowed to cure for a minimum of 24 hr before they were analyzed. Once the samples had cured they were cut out of the mold and were ready for analysis with FTIR-ATR.

The top side of the molded sample—the side that did not come in contact with the mold—was placed on the IRE and then on the ATR accessory. A zinc-selenide (ZnSe) crystal (50 mm × 10 mm × 3 mm) having an incident angle of 45 degrees was selected as the IRE. Before sample placement the crystal was wiped with acetone to remove any residue. A background was run on the ZnSe crystal to eliminate any environmental effects when analyzing the sample spectrum. The cured sealant was pressed against the IRE using a clamping device to maintain a constant path length. All spectra were taken with Nicolet Model 510P Spectrometer using a Michelson Interferometer. Thirty-two scans were used to produce the resulting spectrum, and the resolution was set at 4 cm^{-1} . The system contained a deuterated triglycine sulfate (DTGS) detector, which was purged with dry air to remove moisture and carbon dioxide that might have collected on the optics. All spectra were autobaselined in the absorbance mode before analysis.

The absorbance mode was selected because there is a linear relationship between concentration and the absorption bands. With the bands directly related to concentration, a measure of the area under the band or the band height can be used to measure unknown concentrations.

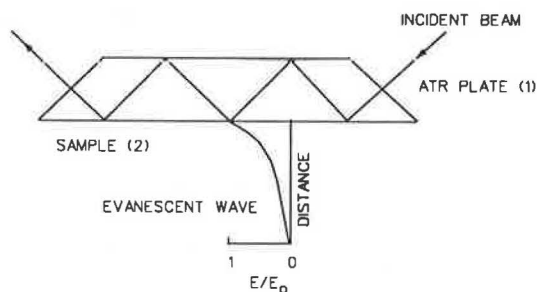


FIGURE 1 Optical diagram of ATR prism showing amplitude decay of evanescent wave (9).

TABLE 1 FEDERAL SPECIFICATION SS-S-200E TEST REQUIREMENTS

TEST	REQUIREMENT
Accelerated Aging, sealed container, 120°F, 21 days Visual	No settling, separation or hardening that will not return to a homogeneous liquid by simple stirring, no skinning greater than 1/16 inch thick
Self-Leveling: Level plane 1.5 percent incline	No flow to a variation of the surface greater than 1/8 inch No flow to a variation of the surface greater than 1/16 inch
Change in Weight by Fuel Immersion, percent	Shall not exceed 2.0 of the initial weight
Change in Volume on Exposure to Elevated Temperature, 158°F, 168 hours, percent	Shall not exceed 5.0 of the initial volume
Resilience: Unaged Initial indentation, (mm) Recovery, percent Aged Initial indentation, (mm) Recovery, percent	0.5 to 2.0 Minimum of 75 0.5 to 2.0 Minimum of 75
Resistance to Artificial Weathering, 140°F, 160 hrs Test panels	(a) No breakdown of cure or reversion of the sealant (b) No blistering or deformation greater than "blister size No. 2" and classed as "medium dense" in accordance with ASTM D 714
Volume change, percent	Shall not exceed 5.0 of the initial volume
Bond to Concrete (-20°F) Nonimmersed	None of the specimens shall develop any surface checking, cracks, separation or other opening in the sealant. No hardness or loss of rubber-like characteristics in the sealant.
Fuel-immersed Water-immersed	Same as Nonimmersed Same as Nonimmersed
Flame Resistance	Shall not support combustion, flow harden or lose adhesive strength
Flow, cm, 5 hrs, 200°F	No cracking or dimensional change
Type M Sealant	(a) Pressurized mixing and extruding equipment shall be used (b) One to one ratio \pm 5 percent by volume of Parts A and B (c) Viscosity, 75 F \pm 5°F Part A 200,000 cP max. Part B 200,000 cP max. (d) Working life to allow ample time for filling joints (e) Tack free time 3 hrs max.
Type H Sealant	(a) N/A (b) Ratio Parts A to B supplied by manufacturer (c) Viscosity, 75 F \pm 5°F Part A 150,000 cP max. Part B 150,000 cP max. (d) Same as Type M (e) Tack free time 12 hrs max.

TABLE 2 WEIGHT RATIOS USED TO MIX TWO-COMPONENT JOINT SEALANTS (LOT 1)

Component A (grams)	Component B (grams)	Component B weight (%)
20.00	0.00	0.00
19.05	15.00	44.05
9.60	15.00	60.98
9.70	25.00	72.98
9.16	50.00	84.52
9.74	100.00	91.10
9.49	150.00	94.00
9.49	160.00	94.40
9.64	200.00	95.40
0.00	20.00	100.00

Effect of Depth on Spectra

Because the ATR technique analyzes from the surface only to a depth of approximately 0.5 to 10.0 microns into the sample (7), the technique may not be analyzing a representative cross section of the material. To determine the effect of depth on composition, samples from the two-component joint sealant were cut in half and spectra were taken of the exposed surfaces. The effect of depth on composition is presented in Table 3. The ratio of the peak heights was found to be relatively independent of depth or cure time after 1 day. This is consistent with the manufacturer's recommended cure time of 24 hrs.

That the ratio of the peak heights is relatively independent of depth is particularly interesting if field samples are to be analyzed. To analyze a field sample, the surface exposed to the environment would have to be removed to prevent dust and the like from affecting the spectrum.

RESULTS AND DISCUSSION

Spectra Interpretation

The two-component joint sealant is a coal-tar modified polymeric material consisting of an accelerator (Component A)

and base (Component B). The bands found to be exclusive to Component A are a broad band from 3600 cm^{-1} to 3200 cm^{-1} from hydrogen bonding of the water and a sharp band at 1736 cm^{-1} from the carbonyl group. Component B contains both the polymer and the coal-tar pitch modifier. Characteristic bands from Component B are observed for the aromatic carbon-carbon double bond at 1599 cm^{-1} and the hydrogen-bonded phenolic (O—H) stretch at 3422 cm^{-1} (8). Several sharp peaks appear from 3694 cm^{-1} to 3620 cm^{-1} from hindered phenol groups. A weak band is also observed at 1919 cm^{-1} from overtones of the strong, broad inorganic bands at 900 cm^{-1} and 1000 cm^{-1} .

To develop a calibration curve, nonoverlapping, noninteracting bands must be selected for each component. The changes in these bands with composition will give a measure of the amount of each component in the mix. Because there is some overlap between Component B bands at 3694 cm^{-1} to 3422 cm^{-1} and the broad band of Component A at 3406 cm^{-1} , they were eliminated from consideration. The absorption band at 1599 cm^{-1} from Component B overlaps with several lesser peaks in Component A. The remaining bands available to develop a calibration curve are the strong band at 1736 cm^{-1} for Component A and the weak band at 1919 cm^{-1} for Component B. These two bands were selected for developing a calibration curve.

Developing the Calibration Curve

The calibration curve was produced by measuring the peak heights from the baseline to the peak maximum of the bands displayed in Figures 2 and 3 for Components A and B, respectively. A series of overlaid spectra are displayed in Figure 4, showing the effect of different weight ratios on the absorption of the two bands for Lot 1. A ratio index was then developed to determine the contributions at different weight ratios. The ratio index is defined by the following equation:

$$\text{Index} = A_{\text{Peakmax}}/B_{\text{Peakmax}} \quad (1)$$

where B_{Peakmax} is the peak height of the band at 1919 cm^{-1} extending from 1980 cm^{-1} to 1835 cm^{-1} representing Component B, and A_{Peakmax} is the peak height of the band at 1736 cm^{-1} extending from 1780 cm^{-1} to 1680 cm^{-1} characteristic

TABLE 3 RATIO INDEX VALUES OF VARIOUS 1:10 (A:B) WEIGHTED SAMPLES AT DIFFERENT CURE TIMES AND DEPTHS OF 0 AND 1.5 mm (AVERAGE RATIO = 6.324, STANDARD DEVIATION = .343)

Time (days)	Depth (mm)	Component A (grams)	Component B (grams)	Component B weight (%)	Ratio Index
1	0	9.31	100.00	91.48	5.859
1	1.5	"	"	"	5.875
4	0	9.57	100.00	91.27	6.465
4	1.5	"	"	"	6.662
6	0	9.32	100.00	91.47	6.368
6	1.5	"	"	"	6.716

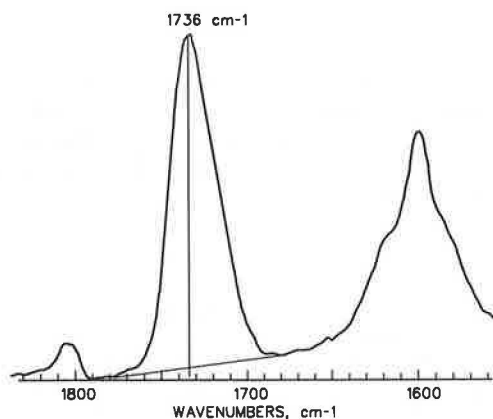


FIGURE 2 FTIR-ATR spectrum of characteristic peak for Component A.

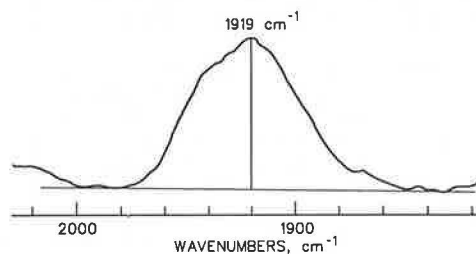


FIGURE 3 FTIR-ATR spectrum of characteristic peak for Component B.

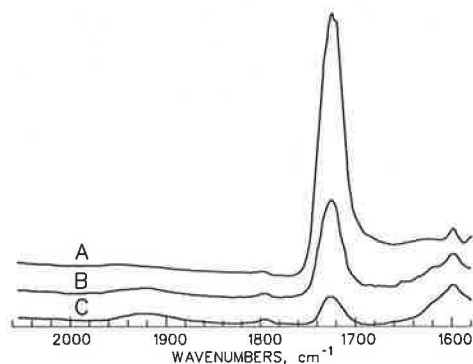


FIGURE 4 FTIR-ATR spectra of two-component joint sealant mixed at following weight percents of Component B: A = 44.05 percent, B = 84.52 percent, and C = 94.40 percent.

of Component A. This ratio index was then plotted against the known weight percent of Component B and is displayed in Figure 5. The resulting curve shows a nonlinear relationship between the ratio index and the weight percent of Component B, suggesting that some interaction is occurring in the two-component system. The different weight ratios will substantially change the degree of cure of the joint sealant, so it is expected that a nonlinear relationship would occur. A second-

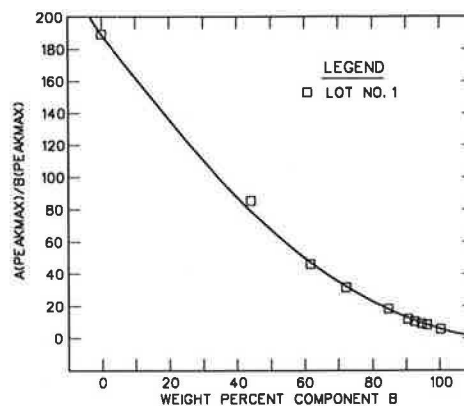


FIGURE 5 Calibration curve for the two-component joint sealant material from Lot 1.

order polynomial was calculated from the data to produce Equation 2.

$$\begin{aligned} \text{Index} = & 6.393 - 0.8119 (\text{weight percent of Component B}) \\ & + 0.01293 (\text{weight percent of Component B})^2 \end{aligned} \quad (2)$$

The second-order polynomial provided an excellent fit with a correlation coefficient of $r = .9989$.

It was first assumed that a linear relationship could be developed between the measured ratio and the actual weight percent of Component B. Because of the curing process in the mixed system, interaction between the components has produced a nonlinear curve. The band used for Component B is from the coal-tar modifier and probably does not change significantly in the presence of Component A; the band selected for Component A is probably directly involved in the curing process. Joint sealant materials are complex chemical systems composed of many different types of chemical compounds. Further research is required to better understand the interactions occurring between these various compounds and how they change with cure time.

Validation of Method

To verify the ability of the calibration curve to determine the mixing ratio of an "unknown" weight percent of Component B sample, another lot number was obtained and mixed in various ratios. The index values calculated from the spectra from Lot 2 were compared to the calibration curve (see Figure 6). It is evident that there is excellent agreement between the ratio index values obtained from the different lot numbers. This suggests that it is possible to develop one calibration curve for each specific joint sealant material.

CONCLUSIONS

1. FTIR-ATR can be a valuable tool for analyzing joint sealant materials with minimal preparation time.

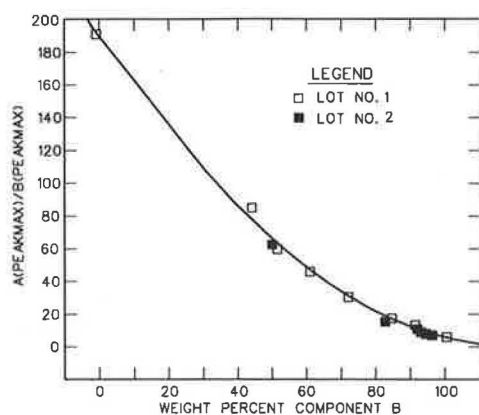


FIGURE 6 Comparison of ratio values measured for known weight percent of Component B for Lot 2 against calibration curve calculated from Lot 1.

2. The work on the coal-tar modified polymeric two-component joint sealant indicates that a calibration curve can be developed to determine the weight percent of an unknown two-component mixed joint sealant sample if a set of known samples exists. This technique could be useful in performing quality control of joint sealant materials mixed at the construction site or in a postconstruction evaluation to determine whether the manufacturer's specified mixing ratio was met.

3. Although the absorption bands selected for the calibration curve were nonoverlapping, there was significant interaction between the two components during the curing process. The interactions produced a nonlinear calibration curve. Joint sealant materials are a very complex system composed of polymers, plasticizers, fillers, pigments, activators, extenders, and base resins. The interaction between the components makes spectrum interpretation very difficult; further work is required to better understand these interactions.

ACKNOWLEDGMENTS

The support of the U.S. Army Engineer Waterways Experiment Station in collecting and preparing material for this paper is gratefully acknowledged. The review and comments of Timothy Vollor, George Hammitt II, Raymond Rollings, and Paul Hadala are greatly appreciated.

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The material presented herein represents the views of the authors only and does not purport to reflect the position of the U.S. Department of the Army or U.S. Department of Defense. This paper was published with the permission of the Chief of Engineers.

Publication of this paper sponsored by Committee on Sealants and Fillers for Joints and Cracks.