

CHARACTERIZATION OF ASPHALTS AND ASPHALT/AGGREGATE MIXTURES USING FLUORESCENCE MICROPHOTOMETRY

Gareth D. Mitchell and Alan Davis
Energy and Fuels Research Center
The Pennsylvania State University
University Park, PA 16802

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INTRODUCTION

Current techniques used in the paving industry for measuring pavement deterioration first require that the asphalt binder be recovered by solvent extraction [1]. This practice may disrupt the molecular structuring that has developed during asphalt aging and which may be responsible for some of the detrimental changes in pavement properties [2]. Fluorescence microphotometry is being developed as a non-destructive quantitative technique for the characterization of asphalt binder quality and deterioration, for both the raw asphalts as well as from cements and pavement cores.

EXPERIMENTAL

Analysis of fluorescence intensity at 600 nm and the measurement of spectral distribution between 510 - 750 nm were performed using a Leitz MPV-II microscope photometer system [3,4]. For both methods light energy from either a high-pressure xenon or mercury-arc lamp was passed through a heat filter (suppressing red and infrared wavelengths) and then through a series of interference filters which defined the appropriate excitation and measuring wavelengths. Analyses were performed using filter combinations utilizing 390-490 nm (blue light) excitation, 510 nm dichromatic beam splitter and 515 nm long-pass barrier filter. The excitation light was reflected by a 510 nm reflection short-pass dichromatic beam splitter and condensed onto the sample through a 50X NPL FLUOTAR air objective. All measurements were made using a dry nitrogen atmosphere to eliminate photooxidation and the total magnification of the optical system was 625 times. The light energy passed back through the dichromatic beam splitter, and a 515 nm long-pass barrier filter blocked any residual reflected excitation light. From this point, the measuring system became significantly different depending upon the desired measurement, i.e., intensity at a single wavelength or spectral distribution.

For measurement of intensity, the fluorescence emission passed through a measurement filter centered around 600 nm (570-630 nm). The optical signal(s) were transformed into electronic signals by an EMI 9558 photomultiplier and amplified. Once the photoelectric system was calibrated to a glass standard of stable fluorescence intensity (uranyl glass), a statistically adequate number of intensity readings were accumulated [4]. For the measurement of relative intensity by wavelength (spectra), fluorescence emissions were passed through a motor-driven Kratos GM200 double-grating monochromator with 20 nm bandwidth, and then to a RCA C31034A water-cooled photomultiplier for measurement. In this system wavelength and intensity were calibrated over the range of visible light and the spectra were corrected with respect to color temperature [5].

Various samples were obtained including twelve raw asphalts from the Materials Reference Library (MRL, [6]) as well as samples of thin-film oven residues (TFOT) and pressure vessel (TFO-PV-Air) aged asphalts from Western Research Institute. Each of these samples were prepared into plug-mount subsamples suitable for microscopy as discussed elsewhere [4]. About 30 plug mounts were made for each raw asphalt. Following a cool-down period (1h), one preparation was analyzed and the remaining subsamples were sealed in foil multilaminate bags in an argon atmosphere and refrigerated at -5°C . For comparison, some asphalt samples were exposed to room conditions (but protected from light) for various periods of time.

Four aggregates were also obtained from the MRL, including RC (high absorption limestone), RD (low absorption limestone), RB (granite) and RJ (gravel). Each aggregate was split and stage-crushed to pass a 200 mesh ($<74\ \mu\text{m}$) screen. Along with these aggregates, particulate ($<1\text{mm}$) teflon was used as an inert-surface additive to determine the effects of dilution. In addition, four fresh asphalts were obtained (AAA-1, AAG-1-2, AAM-1 and ABD) from the MRL for preparation of asphalt/aggregate mixtures or mastics.

Mastics were prepared by forming a 50/50% volumetric mixture of each asphalt and aggregate following the same methodology. About 50 g of each aggregate were dried in an oven at 150°C for 10h. A fresh asphalt was thoroughly heated and homogenized, each aggregate (or teflon) in turn was removed from the oven and, while still hot, an appropriate amount of asphalt was weighed into the aggregate. Mixtures were stirred until all particles were wetted with asphalt ($\sim 5\ \text{min}$). Subsamples of the mixture were then placed into several preheated 2.5 cm diameter steel molds fitted with steel end caps and pressed under 4000 psi using a hydraulic press. While still in their molds, some of the samples were placed in foil multilaminate bags under argon and refrigerated. Other samples were pushed from their molds and the sides and one end covered with masking tape and labelled. The exposed end was lightly ground on 600 grit abrasive paper to reveal interfaces between asphalt binder and aggregate. Samples were allowed to warm to room temperature in a desiccator before analysis.

Fluorometric and spectral analyses were performed on all mastics of a given asphalt on the day following preparation. Fluorescence intensity was determined using the standard set-up. A total of 50 readings was necessary to obtain repeatable mean fluorescence intensity values from the asphalt binder when aggregate materials were present. Spectral analyses were also performed on the asphalt binder portion of the mastics by determining the mean spectra of readings taken from five different areas.

RESULTS AND DISCUSSION

Measurement of mean fluorescence intensity has been shown to provide unique and characteristic values for individual raw (fresh) asphalts [4]. When measurements were made using xenon irradiation in a nitrogen atmosphere the mean intensity of 10 readings were found to be repeatable to within $\pm 0.1\%$. A preliminary evaluation of fluorescence intensity of twelve asphalts with their initial physical and chemical properties revealed a weak correlation with viscosity (at 60°C). Figure 1 shows that fluorescence intensity decreases as viscosity increases. This relationship was independently supported by comparison of the intensity and viscosity values observed for the AAA-1, AAA-2 and AAE asphalts (Figure 1). These asphalts were derived from

the same petroleum source but were manufactured differently. The AAE asphalt was air-blown, which is a technique used to stiffen asphalt, and is accompanied by a rather large increase in viscosity as well as volatile loss and oxidation. As seen in Figure 1, the fluorescence intensity of the AAE asphalt has been significantly reduced compared with the AAA-1 and AAA-2 samples.

The results of spectral analysis showed that 70% of the raw asphalts had their wavelength of peak fluorescence intensity fall between 664 and 672 nm, with two asphalts (AAD-1 and AAE) having slightly lower peaks at about 640 nm and another asphalt (AAK-1) having a significantly lower peak at 544 nm. Generally, all of the spectra show a very rapid rise in fluorescence intensity in the range of 510-530 nm followed by a gentle increase to their respective peak values. Most of the asphalts show a slight decline in intensity for the next 70-100 nm following the peak value and then a sharp decline to zero between 730-760 nm. However, four of the asphalts (AAE, AAG-1-1, AAH-1 and AAK-1) show a sharper decline in intensity following peak fluorescence. Note that the peak wavelength of the AAE asphalt was lower (640 nm) and the spectral distribution narrower compared with the AAA-1 (665 nm) and AAA-2 (670 nm) asphalts.

A comparative study where two asphalts (AAA-1 and AAB-1) were maintained refrigerated in argon (RA-stored) or exposed (Exposed) to room conditions for different durations demonstrates the influence of molecular structuring. Figure 2 shows that fluorescence intensity decreased with increasing exposure to room conditions, whereas very little change was observed when stored under argon in a refrigerator. These tests were performed on samples from which the top millimeter of asphalt was removed before measurement, thereby removing the effects of skin development and surface oxidation [7] and revealing changes that have occurred in the bulk asphalt. Clearly, we believe that fluorescence intensity decreases with increased molecular structuring. Presumably, as asphalt molecules develop an interconnected structure through the development of hydrogen bonding, dipole interactions and Van der Waals forces, the viscosity of the material would increase as well.

The TFOT and TFO-PV-Air tests were used to measure the aging deterioration of asphalts through progressively more severe oxidation. Depending upon the asphalt employed, these tests can result in changes in asphalt viscosity of one to three orders of magnitude. Table 1 gives fluorescence intensity and wavelength of peak fluorescence as they compare to concentration of carbonyl and sulfoxides (as determined by Western Research Institute) oxidation products for four different asphalts. These functional groups represent potential fluorophoric sites, however, as found with air-blown asphalts (AAE), a progressive decrease in fluorescence intensity with increasing severity of aging/oxidation was observed. Upon severe aging (TFO-PV-Air), three of the four asphalts showed a decrease (blue shift) in the wavelength of peak fluorescence and a narrowing of the spectral distribution. As can be seen in Table 1 peak wavelength and concentrations of carbonyl and sulfoxides were more variable (i.e., some increasing, others decreasing) for the TFOT samples.

From the foregoing it appears that both molecular structuring and aging/oxidation decrease the intensity of fluorescence emissions and increase asphalt viscosity. However, this may not be a direct cause-and-effect relationship, but be due to the fact that the chemical changes occurring as a

result of asphalt oxidation or structuring influence both measurements. Figure 2 compares the fluorometric intensity information obtained from molecular structuring and TFOT tests of two asphalts. The figure shows that the fluorescence intensity of the AAB-1 asphalt has decreased to the range of the TFOT test within 80 days, whereas the loss due to molecular structuring of the AAA-1 asphalt has not been as extensive over about the same duration. Fluorometric differences in the setting and aging properties of different asphalts may prove to be extremely valuable for determining the hardening potential and service life of asphalt binders in contact with aggregate materials.

To determine the influences that aggregate materials might have on the fluorometric properties of asphalt binders, a series of mastic samples were prepared. Intensity and peak wavelength values for each are given in Table 2. Generally, these data show that addition of aggregate to a diversity of asphalt binders results in a rapid (within 17 h) and significant decrease in fluorescence intensity. In comparison, a much smaller decrease was observed when teflon was used as the aggregate, suggesting that neutralization of fluorophoric emissions in asphalt binders may be limited in the presence of materials of larger particle size or of relatively inactive surfaces like teflon. The average decrease in intensity was different for each asphalt, but does not differ significantly between aggregate materials. With some variation the wavelengths of peak fluorescence for the AAA-1 and AAM-1 asphalts were not changed significantly by the presence of the aggregates. However, peak wavelength decreased (blue shift) for the ADB and AAG-1-2 asphalts in the presence of aggregate. It must be mentioned that these two asphalts were from the sample petroleum source except that AAG-1-2 has added lime. However, the addition of aggregate to any one of the set of four asphalts results in a narrowing of the spectral distribution in a manner similar to that observed from the aging/oxidation experiments.

Fluorometric intensity analyses were repeated for two of the mastic sets (AAA-1 and AAM-1) and the results are shown in Table 2. Different procedures were used to obtain new samples for testing and these results were compared with results for mastics that were exposed to room conditions. The AAA-1 set of mastics were used to study the influence of storage in argon under refrigeration (RA-Stored) and the results show an average increase of 0.36% intensity for the mastic samples (excluding teflon) following storage. Thus, it appears that somewhat less than 3% of the 35% decrease in fluorescence intensity observed with the addition of inorganic aggregates to the AAA-1 asphalt may result from storage effects and/or measuring variation. A slightly different response was observed from reheating the AAM-1 asphalt. First, there was a relatively large decrease in the fluorescence intensity of the raw asphalt which may be a result of oxidation and/or volatile loss from the asphalt. Secondly, for the asphalt/aggregate mixtures there was mostly a decrease in fluorescence intensity averaging about 0.22% intensity. Therefore, about 2% of the -43% decrease in intensity resulting from the addition of aggregates to the AAM-1 asphalt may be attributed to analytical errors.

When both sets of mastics were exposed to room conditions a significant decrease in fluorescence intensity was observed. On average the mastics made from AAA-1 (Exposed 64 days) lost slightly more intensity than those made with the AAM-1 (Exposed 101 days) asphalt, i.e., 1.74% vs 1.58%. The differences observed in measured intensity among the different mastics are not much

greater than the variation found during the repeat analyses which means that the type of aggregate used in our mastic preparation has much less influence on changes in fluorescence properties compared with the type of asphalt used.

CONCLUSIONS

Fluorescence microphotometry techniques employ optical microscopy to facilitate the differentiation of asphalt binder from aggregate materials thereby eliminating the need to solvent extract the binder for evaluation. In the current research, techniques for the uniform measurement of fluorescence intensity and spectra were developed and applied to the characterization of raw asphalts. Relationships were found between fluorescence intensity values and viscosity as measured in original and laboratory-aged asphalts. As viscosity increases, intensity decreases, a relationship thought to be due to the dependence of both these properties upon oxidation and/or molecular structuring. Fluorescence intensity also decreases significantly upon the mixing of aggregate materials with asphalt, the magnitude of the change being influenced more by the asphalt binder used rather than the aggregate type. Just as observed for raw asphalts, the fluorescence intensity of asphalt binders in contact with different aggregate materials continues to decrease with curing/aging time. Results of this investigation demonstrate that fluorometric measurement of asphalt intensity has potential for use in monitoring asphalt oxidation during manufacturing and plant mixing, pavement curing and as a technique to monitor the deterioration of asphalt pavements that are in service.

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Table 1. Peak Fluorescence and Intensity Changes with Aging

Asphalt Code	Fresh Asphalt				TFOT Aged 163°C/5 hr				TFO-PV-Air Aged 60°C/400 hr 300 psig			
	Intensity at 600 nm	Primary Peak, nm	Carbonyl, abst	Sulfoxides, m/L†	Intensity at 600 nm	Primary Peak, nm	Carbonyl, abst	Sulfoxides, m/L	Intensity at 600 nm	Primary Peak, nm	Carbonyl, abst	Sulfoxides, m/L†
AA0-1	10.06	640	0.04	0.05	4.85	646	0.02	0.06	3.14	622	0.09	0.37
AAG-1-1	28.72	686	0.03	Trace	11.20	640	0.04	0.09	5.22	663	0.25	0.22
AAK-1	2.20	544	0.03	Trace	1.77	549	--	--	1.10	552	0.08	0.32
AAM-1	9.55	668	0.02	Trace	4.72	666	0.04	0.06	2.70	640	0.16	0.12

† Western Research Institute

Table 2. Intensity and Peak Fluorescence Values of Raw Asphalt and Mastics

Asphalt Code	% Intensity Values at 600 nm and Primary (Minor) Peaks in nm											
	Raw		RB-Granite		RC-Limestone		RD-Limestone		RJ-Gravel		Teflon	
	% Intensity	Peak (nm)	% Intensity	Peak (nm)	% Intensity	Peak (nm)	% Intensity	Peak (nm)	% Intensity	Peak (nm)	% Intensity	Peak (nm)
AAA-1	11.72	664 (720)	7.44	665	7.85	677	7.65	670	7.72	665	11.13	664 (719)
RA-Stored	11.53		7.86		7.86		8.02		8.38		10.94	
Exposed	7.56		5.50		5.73		6.39		6.10		7.75	
ABD	20.90	600 (681)	14.15	556 (682)	13.50	552 (683)	12.65	553 (685)	12.86	555 (686)	17.79	598 (682)
AAG-1-2	28.7	686 (631)	16.18	559 (681)	16.83	555 (681)	16.61	558 (684)	15.00	556 (682)	Not Prepared	
AAM-1	9.55	668 (720)	5.23	607	5.62	676	5.66	665	5.40	668	7.44	668 (716)
Reheat	8.84		5.08		5.63		4.94		5.39		7.07	
Exposed	5.66		3.77		3.99		3.84		3.99		5.19	

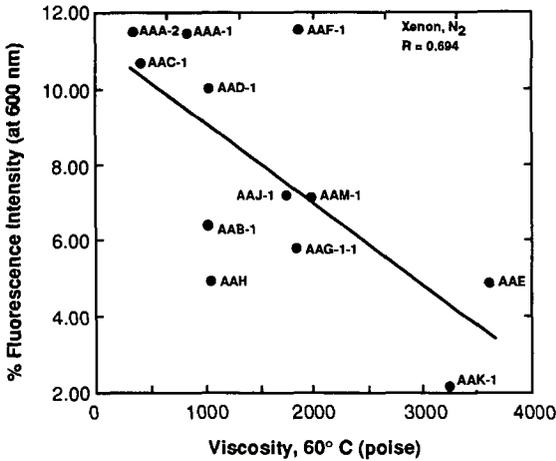


Figure 1. Relationship between Fluorescence Intensity and Initial Viscosity of SHRP Asphalts Measured in Nitrogen Using Xenon Illumination

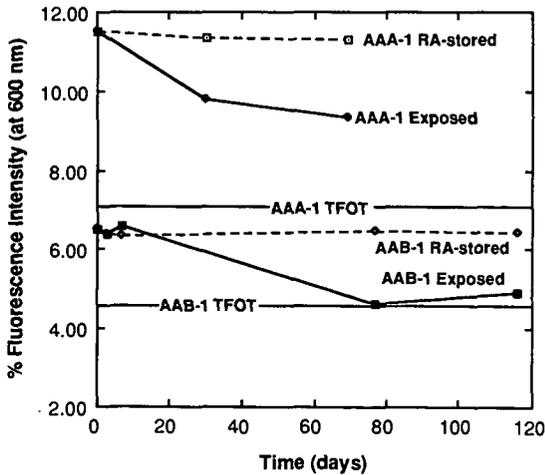


Figure 2. Comparison of Molecular Structuring and TFOT Aging on Fluorescence Intensity of the AAA-1 and AAB-1 SHRP Asphalts