INTRODUCTION
Most of U.S. southeastern states experience both hot and wet summer weather. Extremely high relative humidity and a low dew point maintain a continuous film of water on Gulf Coast roads during the night and early morning hours. Should the laboratory protocols for aging asphalt binders consider the vapors of water as components of the aging atmosphere as well as air (oxygen) exposure? It was the goal of the present investigation to address the potential influence of water on the aging of road pavements containing polymer modified asphalt cements (PMAC).

OBJECTIVE
The objectives of this research were (1) to analyze the properties of a styrene-butadiene-styrene (SBS) block copolymer modified asphalt cement aged in the laboratory in dry and wet atmospheres and a similar PMAC field aged on the road for several years and (2) to develop a criterion for assessing the extent of aging based on laboratory fundamental engineering tests.

SCOPE
This project was sub-divided into two phases: (1) laboratory binder aging and characterization and (2) field binder extraction and characterization. Binder tests were based on a chemical component analysis and Superpave binder characterization that included (1) Fourier transform infrared (FTIR) spectroscopy measurements, (2) gel permeation chromatography (GPC) measurements, and (3) dynamic shear modulus (DSR) and critical gel temperature measurements. The binder of 3-, 5-, and 7-year-old road samples was extracted and analyzed together with the original pressure aging vessel (PAV) PMAC road sample using the same suite of tests for Phase I.

METHODOLOGY
The functional group composition of the binders was examined by FTIR spectroscopy. The acid group content of the asphalts was determined using non-aqueous potentiometric titration. The molecular weight distribution of the asphalt components was estimated using a gel permeation chromatography. A high torque controlled stress AR2000 rheometer was used to determine the complex viscoelastic modulus G* (describing rigidity) of asphalt binders and their critical gel temperature.
A standard SBS polymer modified asphalt cement (PG 76-22M) was selected as a model. Three-, five-, and seven-year-old field aged asphalt samples originally of similar PMAC composition as that of the model PG 76-22 were recovered from a wearing course mixture located on I-55 near Granada, MS. The binder was extracted from pavements with hot toluene. A PAV was used to simulate binder aging during the service life. Thin film oven testing (TFOT) aged samples were submitted to the dry aging step in the PAV at 100°C and 300 psi (1 psi = 6.9 kPa) for 10, 20, 30, and 40 hours. For the wet aging of asphalts, water (50 g) was placed in one pan in the pressure vessel, and the same aging protocol was applied.

**CONCLUSIONS**

Aging was reflected in the infrared spectra of asphalts. The more oxidized the asphalt (e.g., PAV aged), the more intense the 1695 cm⁻¹ peak becomes, and the corresponding 1695/1455 cm⁻¹ ratio increases (Figure 1). The high auto-oxidative sensitivity of PMAC suggests that the polymer additive behaves as a sacrificial antioxidant. When the PMAC sample subjected to TFOT and dry PAV aging was analyzed by GPC, the polymer species from PMAC eluted at a time that corresponded to a molecular weight of 120,000 Daltons. However, the PAV aging process caused a severe oxidation of the PMAC polymer molecules, broadening the polymer peak towards higher elution times, or lower molecular weights. Weathering of the base asphalt cements also results in a significant increase of large molecular size (LMS) species (asphaltenes aggregates) at around 104 Dalton and a significant decrease of medium and small molecular size species.

The combined effects of oxidative aging of SBS and asphalt components (i.e., crosslinking of polymer and aggregation of asphaltenes) led to a higher critical temperature (Tᵥ) at the gel point. Wet aging produced much softer materials with a Tᵥ of samples aged after 70 hrs. aging equivalent to that of dry PAV samples aged for only 30-40 hrs. Critical temperatures of 25-26°C were experienced for pavements 3-5 yrs. old (dry aging) or 5+ yrs. for wet conditions. The results are presented in Figure 2.

FTIR data have shown that multiple PAV aging introduced polar carboxylic acid oxygen species. Aging drastically reduced the molecular mass of SBS polymer and increased the content of LMS asphalt components. A GPC analysis confirmed the degradation of polymeric species to lower molecular weight (MW), while weathering of the base asphalt cements resulted in a significant increase in asphaltene aggregation. Upon aging, the copolymer crosslinked and contracted around the asphaltene aggregates. The combination of these effects with aggregation of asphaltenes led to an increase of the PMAC critical temperature. By calibrating the laboratory aging results with field data, a nomogram can be obtained for assessing the aging of SBS PMAC binders.

**RECOMMENDATIONS**

The procedures used in this project are recommended for forensic analysis of existing pavements to determine levels of oxidation and polymer presence. Forensic analysis of asphalts extracted from aged pavements that were built with well-documented binders and the correlations of results obtained with the contemporary condition of roads will build a data bank based on which new specifications can be developed.