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# The investigation and comparison effects of SBS and SBS with new reactive terpolymer on the rheological properties of bitumen

#### Perviz Ahmedzade\*

Department of Civil Engineering, Ege University, Izmir, Turkey

HIGHLIGHTS

▶ The effect of styrene–butadiene–styrene (SBS) and SBS + Entira®Bond 8 additives on characteristics of bitumen was investigated.

The results showed that both polymers groups reduce temperature susceptibility of bitumen.

▶ SBS + Entira®Bond 8 modifications improved the properties of bitumen better than just SBS modifications.

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#### ABSTRACT

The effects of styrene–butadiene–styrene (SBS) and SBS with new reactive terpolymer (Entira<sup>®</sup>Bond 8) modifications on the rheological properties of pure bitumen were investigated and compared to each other. Four polymer modified bitumens (PMBs) were produced by mixing bitumen with SBS at two polymer contents and with SBS + Entira<sup>®</sup>Bond 8 at the same polymer contents.

The rheologic characteristics of the PMBs were analyzed by means of conventional test methods like penetration, softening point and Fraas breaking point as well as rotational viscometer (RV), dynamic shear rheometer (DSR) and bending beam rheometer (BBR) test methods.

Conventional binder properties of different PMB groups demonstrated that the polymers increase stiffness (hardness) and improve susceptibility of pure bitumen to temperature changes. Both polymers groups improve properties of bitumen, such as increased elastic responses (increased complex shear modulus and decreased phase angle) at low to high temperatures and reduced creep stiffness at low temperatures.

Based on the results of this investigation it can be noted that SBS + Entira®Bond 8 modifications improved the conventional and more fundamental properties of bitumen better than just SBS modifications.

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ERIALS

#### 1. Introduction

An asphalt concrete road consists of a choice of different sizes of aggregate held together by bitumen. The bitumen only makes up 5–7% by weight or approximately 15% by volume of the asphalt concrete mix. Despite this small percentage, the performance of the bitumen has a significant influence on the long term performance of a road. The bitumen used in flexible pavements exhibits elastic behavior at low temperatures and under high speed vehicles where as viscous behavior at high temperatures and under low speed vehicles. Under normal conditions and intermediate temperatures, the bitumen shows viscoelastic behavior.

In order to accommodate increasing traffic loadings as well as resist temperature changes, specific polymer based additives are utilized. Pavement with polymer modification exhibits greater

\* Tel.: +90 533 7212423; fax: +90 232 3425629.

E-mail address: perviz.ahmedzade@ege.edu.tr

resistance to rutting and thermal cracking, and decreased fatigue damage, stripping and temperature susceptibility. Polymer modified binders have been used with success at locations of high stress, such as intersections of busy streets, airports, vehicle weigh stations, and race tracks [1–5].

Among these additives, the most commonly used polymer is elastomeric type styrene-butadiene-styrene (SBS) copolymer. SBS copolymers consist of block segments of styrene monomer units and butadiene rubber monomer units. Each block segment can consist of many monomer units. The most common form used in bitumen modification is a linear styrene-butadiene-styrene structure, but radial types are also available.

The content, structure of SBS, structure of base bitumen as well as the mixing time and temperature are important factors that should be taken into account in the production of SBS polymer modified bitumen (PMB). Recent studies indicate that pavement with SBS polymer modification exhibits greater resistance to

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Table 1

Properties of the base bitumen.

Test	Specification	Results	Specification limits
Penetration (25 °C; 0.1 mm) Softening point (°C)	ASTM D5 ASTM D36	130 45.7	100–150 39–47
Fraas breaking point (°C)	IP 80	-20	max–12
Penetration index (PI)	-	0.33	-

permanent deformation at hot climates, cracking at low temperatures and fatigue cracking due to the increased bitumen stiffness [6–9].

The temperature is an extremely important factor in the structure of the SBS polymer modified bitumen. After production, care must be taken in order to hold the polymer modified bitumen under constant temperature since the SBS can be easily decomposed from the base bitumen and is not appropriate for storage. Not holding the final product under required level of temperature can lead to adhesion, decomposition and frost problems. Besides the SBS is an expensive additive.

In order to raise the efficiency of bitumen modification, to decrease the production cost as well as to increase the storage stability properties of SBS modified bitumens without additional heating procedures, DuPont Company produced a new reactive terpolymer (Entira®Bond 8) to be used with SBS. The utilization of the Entira®Bond 8 decreases the SBS polymer consumption by almost 50% which makes this additive a cost effective polymer [10]. This study aims to investigate and compare effects of SBS and SBS with Entira®Bond 8 on the rheologic properties of bitumen.

#### 2. Experimental

#### 2.1. Materials

The base bitumen with a 100/150 penetration grade has been procured from Turkish Petroleum Refineries Corporation (TUPRAS). Table 1 gives a summary of the results of some tests performed on the base bitumen.

The SBS polymer used was Kraton D-1101 supplied by the Shell Chemicals Company. Kraton D-1101 is a linear SBS polymer in powder form that consists of different combinations made from blocks polystyrene (31%) and polybutadiene of a very precise molecular weight [11]. These blocks are either sequentially polymerized from styrene and butadiene and/or coupled to produce a mixture of these chained blocks. The reactive terpolymer Entira<sup>®</sup>Bond 8 was provided by DuPont Company.

#### 2.2. Preparation of samples

The SBS Kraton D-1101 concentrations in the base bitumen were chosen as 3% and 4.5% by weight. In preparation, the base bitumen was heated to fluid condition (180–185 °C), and has been poured into a 2000 ml spherical flask. Then the SBS polymer was added slowly to the base bitumen. The SBS modified bitumen samples were prepared by means of laboratory type mixer rotating at 500 rpm. On reaching temperature of 190 °C, the temperature has been kept constant and the mixing process continued for 2 h.

The SBS Kraton D-1101 concentrations in the base bitumen replaced half of the SBS polymer contents (1.5% and 2.25%) and then Entira®Bond 8 was added to SBS modified bitumens to prepare SBS with Entira®Bond 8 modified bitumen samples.

Concentration of Entira<sup>®</sup>Bond 8 was chosen as 1% according to the manufacturers (DuPont Company). Conditions of preparing process of SBS with Entira<sup>®</sup>Bond 8 modified bitumen specimens such as temperature, speed and time of mixing used were the same as in preparation of SBS modified bitumen samples. After complete blending for 2 h, the blended samples were cured for 2 h at 190 °C to achieve chemical reaction which allowed to create permanently modified binders.

The uniformity of dispersion of polymers in the base bitumen was confirmed by passing the mixture through an ASTM 100# sieve. After completion, the samples were removed from the flask and divided into small containers, covered with aluminum foil and stored for testing.

The different binders were coded as follows:

- base bitumen "B";
- base bitumen + 3%SBS "B-3S";
- base bitumen + 1.5%SBS + 1% Entira®Bond 8 "B-1.5S-1E"
  base bitumen + 4.5%SBS "B-4.5S";
- base bitumen + 2.25%SBS + 1% Entira®Bond 8 "B-2.25S-1E".
- 2.3. Testing program

#### 2.3.1. Conventional bitumen tests

The unmodified and modified bitumens were subjected to the following conventional bitumen tests: penetration, softening point and Fraass breaking point. In addition, the temperature susceptibility of the modified bitumen samples has been calculated in terms of penetration index (PI) using the results obtained from penetration and softening point tests. Temperature susceptibility is defined as the change in the consistency parameter as a function of temperature. A classical approach related to PI calculation has been given in the Shell Bitumen Handbook [12] as shown with the following equation:

$$PI = \frac{1952 - 500 \times \log(\text{Pen}_{25}) - 20 \times \text{SP}}{50 \times \log(\text{Pen}_{25}) - \text{SP} - 120}$$
(1)

where,  $\text{Pen}_{25}$  is the penetration at 25  $^\circ\text{C}$  and SP is the softening point temperature of bitumen.

#### 2.3.2. Rotational viscosity test

The rotational viscometer determines the bitumen viscosity by measuring the torque necessary to maintain a constant rotational speed of a cylindrical spindle submerged in a bitumen specimen held at a constant temperature, as per the AASH-TO TP48 standard test method. Unlike the capillary viscometers used with the viscosity-graded method, the rotational viscometer can evaluate modified bitumen binders [13]. The viscosity of bitumen binders can be measured within the range of 0.01 Pa s (0.1 poise) to 200 Pa s (2000 poise) [14]. The Asphalt Institute recommends taking the first viscosity measurement at 135 °C, and the second at 165 °C. A Brookfield viscometer (DV-III) was used for the viscosity tests on the base and modified bitumens.

#### 2.3.3. Dynamic shear rheometer test

The dynamic shear rheometer (DSR) was adopted to characterize the viscoelastic behavior of bitumen binders at low and at intermediate to high service temperatures. The DSR provides an indication of the rutting resistance of bitumen immediately following construction. Resistance to rutting at high service temperatures in the early stages of payement life is also evaluated [15.16].

The DSR evaluates the behavior of a bitumen specimen by subjecting it to oscillatory (sinusoidal) stresses. The AASHTO TP5 standard test method requires that a thin bitumen specimen be sandwiched between two parallel metal plates held in a constant temperature medium. One plate remains fixed while the other oscillates, at an angular frequency ( $\omega$ ) of 10 radians per second for 10 cycles, with respect to the other. A complete DSR loading cycle is shown in Fig. 1 [15].

When torque from the DSR motor is applied, the oscillating plate moves from point A to point B. The plate then passes back through point A to point C. The cycle of oscillation is completed as the plate passes back through point A again. The spin-



Fig. 1. Configuration and load cycle of dynamic shear rheometer [15].

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