



Preventing of rutting and crackings in the bituminous mixtures by monoethylene and diethylene glycol based synthetic polyboron compounds



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HIGHLIGHTS

- Monoethylene and diethylene glycol based polyboron compounds were synthesized.
- Additives have been used as modifying agent for bitumen.
- The effects of additives were evaluated through conventional and superpave test methods.
- Diethylene glycol based polyboron can be used for modified bitumen in hot climates.
- Monoethylene glycol based polyboron can be used for the bitumen in cold zones.

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ABSTRACT

This study deals the modification of bitumen with two new materials, monoethylene glycol based polyboron compound (MEGPC) and diethylene glycol based polyboron compound (DEGPC). These compounds were synthesized chemically and used separately as an additive within the 50/70 penetration grade bitumen. Evaluations about modified bitumens were built on the results of conventional tests (softening point test, Marshall test, Nicholson stripping test) and superpave methods (rotational viscosity, Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR)). The effects of additive concentration on the viscosity were detected at different test temperatures firstly and amount of each additive to be used in the bitumen were chosen as 2% (w/w). The softening point of the bitumen was increased by DEGPC and a slight decrease was obtained by MEGPC modifications. Marshall tests have showed that stability of the bituminous mixtures was improved by both of the additives. Better low temperature cracking resistance and stripping resistance were provided by addition of MEGPC to the original bitumen by means of BBR and Nicholson stripping test results, respectively. Rutting resistance of the original bitumen was enhanced by DEGPC modification according to the DSR test results.

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1. Introduction

Bitumen is a material that is adhesive, colloidal, consisting mainly of hydrocarbons, dark brown to black in colour and can be found naturally or obtained by refining of crude oil in refinery. It is preferred to use in coating courses of flexible pavements (wearing course, binder course) according to its adhesive, water proofing and rheological properties. Bitumen binds the aggregates, as well as supplies stability, durability, flexibility and waterproofing properties to the pavement. Various distresses such as deformations and crackings can be formed in flexible pavements due to the traffic, environmental and climatic effects. Rutting

(deformation type) and low temperature cracking (cracking type) are serious distresses occurring in flexible pavements. In hot regions the rutting risk and in cold regions the cracking risk of the pavement increases. The reasons for the formation of these distresses are closely related with the properties of the bitumen. Preventing or minimizing of distresses will reduce the maintenance cost and enhance the quality of highway transportation. Therefore, studies about improvement of bitumen properties by modification are carried out.

Different additives having various structural properties are available to modify bitumens. Thermoplastic plastomers, thermoplastic elastomers, chemical modifiers, adhesion agents and thermosetting polymers are the modifying agents which are generally used in this doping procedure [1]. Gonzales et al. had reported that improved viscoelastic properties, decreased cracking and rutting

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risks were obtained by the modification of the bitumen with EVA (Ethylene-Vinyl-Acetate) polymer [2]. Besides, the stiffness, thermal resistance of the bitumen and Marshall Stability of the bituminous mixtures were increased by EVA modification [3]. Better cohesion and flexibility, upgraded rutting and deformation resistances are provided by PE and PP (polyethylene and polypropylene) modifications [4]. Jun et al. had reported that rutting resistance of the bitumen was increased by low density polyethylene modification [5], and it was experimentally determined that high density polyethylene had enhanced the rheological properties, as well [6]. Rheological properties of the bitumen were affected by polytetrafluoroethylene modification [7]. Rubber modified bitumen has more resistance to rutting and low temperature cracking [8,9]. Navarro et al. also reported that rubber had improved viscoelastic characteristics of the bitumen, therefore more resistance to rutting and low temperature cracking should be expected [10]. The adhesion [11,12], rutting resistance [13,14], ageing resistance [15], of the bitumen and also the Marshall Stability of the bituminous mixtures [12,15,16] were enhanced by SBS (Styrene–Butadiene–Styrene) modification. Bituminous mixtures prepared with sulphur modified bitumens have better Marshall Stability [17]. Both the bitumen and the bituminous mixture properties were improved by triethylene glycol based polyboron [18]. Zhang and Yu stated out that addition of polyphosphoric acid, SBR (Styrene–Butadiene–Rubber) and sulphur in an optimal ratio might improve the properties of the bitumen [19]. Addition of hydrated lime to the aggregate mixtures decreases the water susceptibility and improves the resistance of bituminous mixtures against aquatic effects [11,20]. Çubuk et al. had manifested that epoxy resin modified bitumen could decrease rutting, bleeding, stripping and cracking problems. In the same study, it was determined that epoxy resin modified bitumen had improved the Marshall Stability of the bituminous mixtures [21].

The purpose of this study was to investigate separately the effects of monoethylene glycol and diethylene glycol based synthetic polyboron compounds on the bitumen and bituminous mixtures by means of conventional (softening point test, Marshall Stability test, Nicholson stripping test) and superpave methods (Rotational viscosity, Dynamic Shear Rheometer, Bending Beam Rheometer).

2. Materials and methods

2.1. Bitumen

The original bitumen with 50/70 penetration grade was supplied from Turkish Petroleum Refinery Corporation and used in all modification applications. Properties of the original bitumen according to the related specifications were presented in Table 1.

2.2. Aggregate

Bituminous mixtures were prepared with 100 percent crushed basalt aggregate. The aggregate was supplied from Gençosman quarry of Sakarya/Turkey. Aggregate gradation for Marshall specimens has been chosen as the average values of Type II wearing course gradation limits of Turkish State Highway Specification. Gradation, physical and chemical properties of the aggregate were given in Table 2.

Table 1
Properties of the original bitumen.

Property	Value	Standard
Specific gravity, 25 °C	1.02	ASTM D-70
Viscosity		
130 °C, (Pa s)	0.316	ASTM D-4402
140 °C, (Pa s)	0.193	ASTM D-4402
Softening point, (°C)	48.4	ASTM D-36
Ductility, 15 °C (cm)	63.5	ASTM D-113

Table 2
Gradation, physical and chemical properties of the aggregate.

Property	Value
<i>Aggregate gradation (passing from each sieve, %)</i>	
(3/4)"	100
(1/2)"	88.5
(3/8)"	75
No 4	56
No 10	40
No 40	20
No 80	12.5
No 200	7
<i>Specific gravity (coarse aggregate)</i>	
Bulk	2.825
Apparent	2.860
<i>Specific gravity (fine aggregate)</i>	
Bulk	2.832
Apparent	2.866
<i>Specific gravity (filler)</i>	
Bulk	–
Apparent	2.833
<i>Water absorption (%)</i>	
Coarse aggregate	0.44
Fine aggregate	0.42
<i>Chemical content (%)</i>	
SiO ₂	1.6
Al ₂ O ₃	0.85
Fe ₂ O ₃	0.57
MnO	0.03
MgO	21.50
CaO	29.67
Na ₂ O	0.10
K ₂ O	0.25
CO ₂	45.45
Cl	0.006
SO ₄	0.002

2.3. Preparation of additives

The additives, monoethylene glycol based polyboron compound (MEGPC) and diethylene glycol based polyboron compound (DEGPC), were synthesized chemically at laboratory conditions. In the synthesis of MEGPC and DEGPC, monoethylene glycol and diethylene glycol were used, respectively. The purities of glycols, bought from Merck, are ≥99%. Boric acid (purity ≥99%), supplied from Eti Mine Works, was reacted with ethylene glycols (mono- or di-) in the presence of catalyst (H₂SO₄). Therefore, synthesized additives were firstly called as polyboric compounds.

Synthesis of additives were carried out under controlled temperature conditions with a simple equipment group composed of a mantle heater with magnetic stirrer, a reactor and a reflux condenser. 150 g ethylene glycol (monoethylene glycol for MEGPC, diethylene glycol for DEGPC) was put into the reactor and started to heat. Immediately after the starting of heating, 0.75 ml H₂SO₄ was added to the ethylene glycol and mixed with magnetic stirrer. While the mixture's temperature reached to 70 °C, 90 g boric acid was added gradually. Mixing-heating processes were continued meanwhile. Temperature was kept constant at 120 ± 2 °C and mixing process was continued for 30 min. At the end of the mixing process the system was wholly switched off and the additive was cooled to ambient temperature then it was hermetically kept into the jar to use in modification of the bitumen.

The MEGPC and DEGPC modified bitumen samples were produced by adding the additive (MEGPC or DEGPC) to the original bitumen which was pre-heated at 110 °C and then mixed in an oil bath at 110 °C for 5 min with a mechanical four-armed mixer rotating at 1300 rpm. MEGPC and DEGPC were added to the original bitumen separately in the following concentrations: 1% (w/w), 2% (w/w), 3% (w/w), 5% (w/w). Viscosity tests were applied to the original and modified bitumen samples in accordance with ASTM D 4402 using Brookfield DV-III rheometer and spindle no. 29. Softening point (ASTM D 36), measure of the temperature susceptibility of bitumen, was measured with EL46-4502 model ring and ball apparatus. DSR, a superpave test method, was performed using Gemini Rheometer (Bohlin Instrument) to determine complex shear modulus and phase angle values for all bitumen types (original and modified) according to AASHTO T315. Creep stiffness and creep rate values (superpave criterions for low temperature properties of bitumen) of the original and modified bitumens were researched according to AASHTO T313 by means of Thermoelectric BBR Instrument (Cannon). Effects of the additives on the mechanical properties of the bituminous mixtures were evaluated with Marshall test and Nicholson stripping test. Marshall test was performed in accordance with ASTM D 1559. Marshall Specimens were prepared using original and

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