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Polymer modified bitumen: Rheological properties and structural characterization

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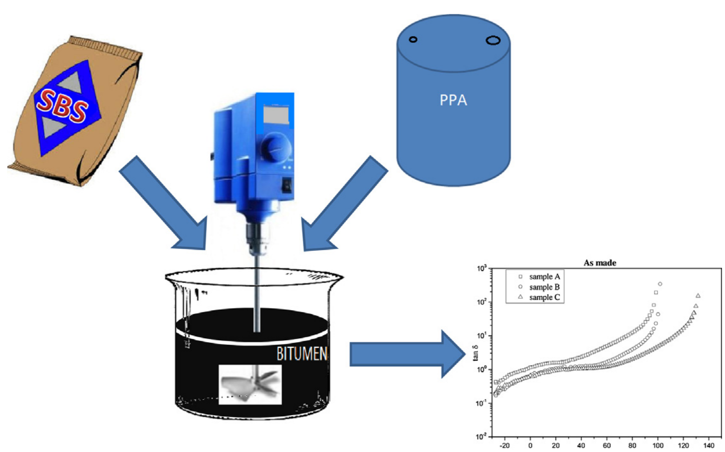
HIGHLIGHTS

- We investigate the effects of SBS polymer and PPA on the structure of the bitumen.
- We examine changes in structures of the bitumen at different aging steps.
- ILT analysis of the NMR echo is one of the most powerful tools for the bitumen structure characterization.

GRAPHICAL ABSTRACT



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ABSTRACT

Polymer modified bitumen (PMB) is used extensively in thin asphalt surfacing and seals in order to improve specific performances. However, the performances of PMB are not easy to demonstrate with the conventional methods, such as penetration test, softening point etc. In order to a better evaluation, different characterization methods are needed rather then ordinary empirical rheological tests. This work deals with the characterization of linear copolymer styrene–butadiene–styrene (SBS) and SBS + polyphosphoric acid (PPA) modified bitumen by using conventional as well as advanced methods on bitumens at different ageing steps and temperature. Fundamental rheological tests, based on a state of the art dynamic shear rheometer in the temperature range from −30 °C to +160 °C and advanced ^{1}H magnetic resonance relaxometry analysis to evaluate the effect of modifiers on the bitumen structure, were used. Moreover, morphological analysis by scanning electron microscope (SEM) was performed on neat and modified bitumen and the effect of the filler addition on the supra-molecular organization of the bituminous binder was also investigated.

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1. Introduction

Bituminous binders are organic materials whose binding and hardening properties are caused by the temperature-related change of adhesion and cohesion of their molecules [1]. Bitumen is often characterized by its chromatographic fractions, the maltenes (saturates, aromatics and resins) and the asphaltenes, soluble and insoluble in *n*-heptane respectively [2], being commonly modeled as a colloid, with maltenes as the continuous phase and micelles of asphaltenes stabilized by associated resins as the dispersed phase [3]. Composition and the colloidal structure determine its physical and rheological properties [4]. These binders are commonly used in the pavement constructions to meet the raising requirements for durability of the road surface [5,6].

A wide range of viscoelasticity is essential to achieve long-lasting road surface, as it ensures consistency of bitumen's rheological state in extreme service temperatures. Modifiers applied for improving bitumen's viscoelasticity are [1]: elastomers, plastomers, synthetic resins, crumb rubber, metal-organic compounds, sulfur, natural asphalts and paraffins. In particular, polyphosphoric acid (PPA) can be used for this purpose.

Currently, the most used modifiers for bitumen performance improvement are long chained hydrocarbon polymers [7]. The physical chemical properties of the polymers modified bitumen (PMB) are dominated by the properties of the base bitumen. Moreover, elastomers increase the elasticity of the bitumen at high temperature and reduce the stiffness at low temperature: both the linear and radial styrene–butadiene–styrene (SBS) copolymers are the most used. In the bitumen, SBS forms a highly elastic network that disappears above 100 °C and reforms when cooled.

Addition of PPA to the binder results in an increase of softening point with no effect (or sometimes small decrease) on low-temperature brittleness [8], as PPA does not oxidize asphalt. This leads to an improvement of the maximum service temperature (or useful temperature range). Since 1990s, research on using PPA in conjunction with polymers to improve quality of road bitumens has been conducted. The major benefit of this particular combination is synergistic effect – possible reinforcement of both modificators effects on asphalt. It has been observed for binder elasticity, thermal cracking resistance, and resistance to permanent deformation [9]. Moreover, PPA improves adhesion and may eliminate the need for antistripping agents. In addition, the stability of binder during long-time storage at elevated temperatures is increased. Overall cost of using modified asphalt binders is reduced by using fewer modifiers, possible elimination of antistrips, and energy savings from lowering operating temperatures [9]. Addition of PPA may reduce reaction time with some polymers [8]. Polymers linked with PPA are: SBS [10–13], ethylene vinyl acetate [10,12] and ethylene terpolymer [14].

On this background, this paper is focused on the deeper understanding of the behavior of bitumen and the effects of polymer based additives on bituminous systems, in order to correlate the macroscopic properties to the microstructure of the aggregates that constitute the colloidal network. In particular, neat, SBS and SBS + PPA modified bitumens have been investigated by using dynamic rheological tests carried out in linear viscoelastic conditions. The rheological properties were further compared with the results of the empirical methods (ring and ball and penetration depth tests) evidencing the potential failures of both methods and looking for potential parameters able to quantify the relationships between mechanical properties and modifications induced by SBS and SBS + PPA. We further used advanced characterization methods such as time-domain nuclear magnetic resonance (TD-NMR) of ^{1}H nuclei, scanning electron microscopy (SEM) and Rheology.

SEM was used to better investigate the morphological structure of unmodified and modified bitumens. While with TD-NMR, we exploited the spin-spin relaxation time (T_2) measurement to find the soften point of neat and modified bituminous materials to understand the morphology of the colloidal bitumen. To this purpose, the Inverse Laplace Transform (ILT) of the NMR spin-echo signal decay was used to obtain T_2 relaxation time distributions of bitumen both at different temperatures and at aging steps. That provided us indications on the nature of the interaction between additives and the colloidal network. Hence, in the present study, we have quantitatively evaluated the effect of the modifiers combining the results of TD-NMR measurements and bidimensional micro-scale scanning electron microscopy.

Table 1
Technical data.

Polymer Properties	Value	Test method
Viscosity of Toluene solution at 25%	5 Pa s	MA 04-3-064
Viscosity of Toluene solution at 5.23%	13 cSt	MA 04-3-003
Volatile matter	0.4%	ASTM D-5668
Hunterlab color	2	ASTM D-1925-70
Total styrene (on polymer)	31%	ASTM D-5775
Hardness	76 Shore A	ASTM D-2240
Insolubles in toluene, 325 mesh	<0.1, %	MA 04-3-018
Ashes	<0.35%	ASTM D-5669

2. Experimental

2.1. Chemicals and materials

The bitumen used in this study has been produced in Kazakhstan and it was supplied by Kazakhstan Highway Research Institute (Almaty, Kazakhstan). It has a 90/130 penetration grade. The bitumen was modified with linear SBS (commercial name, Calprene®501) and with PPA. Calprene®501 is a 69/31 butadiene/styrene thermoplastic copolymer, polymerized in solution and having a linear structure.

The properties of the polymer are presented in Table 1.

Polyphosphoric acid, 83.3% P_2O_5, or otherwise stated 115% H_3PO_4 equivalent [15], has been provided by ICL Performance Product LP (St. Louis, MO, USA).

2.2. Sample preparation

The first step was dedicated to prepare the polymer modified bitumen, by using a high shear mixing homogenizer (IKEA model). Firstly, bitumen was heated up to 180 ± 5 °C until it flowed fully then a given part of SBS (4% of the weight of the base bitumen) was gradually added (5 g/min) to the melted bitumen under a high-speed shear mixer of 5500–6000 r/min. Furthermore, the mixture was stirred by a mechanical stirrer at 180 °C for 2 h while the rotation speed of mechanical stirrer was 300 r/min so that the blends became essentially homogenous. The PPA was added to polymer modified bitumen at a level of 0.2% by weight at 180 °C. The mixture was heated and maintained at 180 °C and continuously mixed at 5500–6000 r/min for 30 min in a closed beaker to avoid any oxidation process. After mixing, the resulting bitumen was poured into a small sealed can and then stored in a dark chamber thermostated at 25 °C to retain the obtained morphology.

2.2.1. Aging

All samples are exposed to two aging steps:

RTFOT: According to ASTM D2872-04, simulation of bitumen aging was done by Rolling Thin-Film Oven Test (RTFOT). Accordingly, a moving film of bitumen was heated in an oven for 85 min at 163 °C.