



# Influence of emulsification on the properties of styrene–butadiene–styrene chemically modified bitumens

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## ABSTRACT

The effect of emulsification on the styrene–butadiene–styrene (SBS) chemically modified bitumens (CMBs) is studied by conventional tests, differential scanning calorimetry (DSC) and fourier transform infrared (FTIR) spectroscopy. Compared to CMBs, modified bitumen emulsion residues (MBERs) exhibit higher temperature susceptibility, inferior resistant to cracking and deformation, lower elastic recovery and storage stability whereas these properties are improved substantially relative to base bitumens. DSC results show that the thermostability of CMBs decreased slightly after emulsification which indicate the emulsification exerts very little effect on the thermal property of CMBs. The FTIR results do not indicate any chemical reaction exists on CMBs during the emulsification.

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## 1. Introduction

It has been known for some time that polymer modified bitumen can be utilized to achieve good pavement performance [1]. In such bitumen, the polymer acts both as an elastomer and a thermoplastic provider part; enabling improved performance with respect to pure bitumen [2]. Styrene butadiene styrene (SBS), in particular is one of the most commonly used modifying component; attributable to its thermoplasticity at high temperatures (useful to avoid permanent deformation) as well as its elasticity at low temperatures (useful to improve resistance to cracking) [3,4].

In recent years, concurrent with the demands towards safer and more environmentally friendly materials, substantial research and development efforts have been devoted to the emulsification of polymer modified bitumen [5,6]. However, it is generally difficult to obtain stable emulsion (using such normal modified bitumen) which can withstand particles aggregation and precipitation over long period of time due to their thermal instability and large sizes of SBS particles. To this end, a cross-linking agent can be used to promote reaction between SBS and bitumen to produce SBS chemically modified bitumen. Normally, the agent is a vulcanized substance containing active groups which connect the unsaturated C=C band of SBS and heteroatom of bitumen to form cross-linking and grafting reactions. Thus, SBS is dispersed uniformly (in bitumen) via chemical bonds within three-dimensional network

structure. This in turn makes emulsification possible so that better thermostability and smaller size of SBS particles can be achieved.

Further on, the properties of SBS modified bitumen emulsion depend on its residue's properties. The residue is normally less useful (relative to modified bitumen) since it originates from the emulsification of modified bitumen. Of interest is the impact of residue's properties toward the curing process. Despite the availability of numerous characterization techniques, such as differential scanning calorimetry (DSC) [7–12] and fourier-transform infrared (FTIR) spectroscopy [10,12–14] to measure the properties of modified bitumen, there is not many systematic studies utilizing these two techniques to probe change in the properties of modified bitumen during emulsification.

The objective of this work is to investigate the effect of emulsification on the properties of CMBs. Properties of CMBs and modified bitumen emulsion residues (MBERs) were probed using several different conventional testing techniques (e.g. penetration, softening point, ductility, elastic recovery and penetration index), DSC and FTIR spectroscopy.

## 2. Materials and methods

### 2.1. Materials

Three base bitumens (AH-70), Zhonghai (China National Offshore Oil Corp.), Caltex (Caltex Oil Corp.) and SK (SK Oil Corp.) were modified with a SBS copolymer and a cross-linking agent to produce three CMBs (named as  $M_z$ ,  $M_c$  and  $M_s$  which correspond to bitumens of Zhonghai, Caltex and SK respectively). The properties of base bitumens are presented in Table 1.

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**Table 1**  
Properties of base bitumens.

Items	Zhonghai	Caltex	SK	Specification
Penetration (25 °C, 0.1 mm)	65	67	63	GB/T 4509
Softening point (°C)	47.6	45.9	46.7	GB/T 4507
Ductility (5 °C, cm)	5	2	7	GB/T 4508
Penetration index (PI)	−1.22	−1.62	−1.54	–

The SBS polymer, LCY 3501 (LCY Chemical Corp.), is a linear SBS copolymer; consisting of different combinations of blocks polystyrene (32%) and polybutadiene (68%) with very precise molecular weight. The cross-linking agent and emulsifier (MQK-1M) were provided by PetroChina LiaoHe Asphalt Co., Ltd. and Meadwestvaco Corporation, respectively.

### 2.2. Preparation of modified bitumen emulsion

The CMB was prepared by mixing SBS (3% by weight) and cross-linking agent (0.3% by weight) into the base bitumen under high shearing at 170–175 °C for 1 h. The mixture was then stored at 170–175 °C in an oven for 1 h. Finally, the CMB was pumped into mill (Daiworth Machine Products, Inc.) and mixed with the heated emulsifier solution (62% by weight of CMB and 38% by weight of solution). Modified bitumen emulsion samples were taken after steady-state is reached.

### 2.3. Recovery of MBER

The MBER was obtained by drying 300 g of modified bitumen emulsion sample at atmospheric temperature to completely evaporate the contained water. During the process, the temperature was kept below 163 °C to prevent the MBER to age. Three MBERs were named as  $M_{ZR}$ ,  $M_{CR}$  and  $M_{SR}$  respectively, to keep consistent with CMBs,  $M_Z$ ,  $M_C$  and  $M_S$ .

### 2.4. Test methods

#### 2.4.1. Conventional bitumen tests

Ring and ball softening point, penetration, ductility at 5 °C, elastic recovery and storage stability of CMBs and MBERs were tested according to specifications listed in Table 2.

The temperature susceptibility of the CMBs and MBERs samples was measured in terms of penetration index (PI) using the results obtained from penetration and softening point tests. A classical approach related to PI calculation was given in the shell bitumen handbook [15], represented by the following equation:

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

where  $\text{Pen}_{25}$  is the penetration at 25 °C and  $T_{SP}$  is the softening point temperature of the specimens.

#### 2.4.2. Thermal analysis

The DSC was performed on a NETZSCH DSC 204 F1 calorimeter with a heating rate of 10 °C/min. Nitrogen gas was used as the purge gas at a flow rate of 20 mL/min.

#### 2.4.3. Microstructure characterization

The FTIR spectroscopy was conducted on a Nicolet IS 10 equipment. Qualitative analysis of samples in chloroform was measured through thin wafers with potassium bromide (KBr) at wave number between 4000  $\text{cm}^{-1}$  and 400  $\text{cm}^{-1}$ .

**Table 2**  
Properties of CMBs and MBERs.

Items	$M_Z$	$M_{ZR}$	$M_C$	$M_{CR}$	$M_S$	$M_{SR}$	Specification
Penetration (25 °C, 0.1 mm)	48	54	63	63	54	52	GB/T 4509
Softening point (°C)	59.5	55.0	79.9	74.1	82.0	75.9	GB/T 4507
Ductility (5 °C, cm)	20	17	32	25	32	21	GB/T 4508
PI	0.82	0.16	4.96	4.13	4.80	3.85	–
Elastic recovery percentage (%)	86	75	96	91	90	87	SH/T 0737
Storage stability (°C)	1.3	2.4	0.5	1.1	1.5	2.1	SH/T 0740
Four fractions							
Saturates (S, %)	17.3	16.6	11.4	11.7	12.3	12.9	SH/T 0509
Aromatics (A, %)	30.1	31.6	47.1	44.8	47.0	43.1	SH/T 0509
Resins (R, %)	45.5	44.9	31.2	33.1	24.9	28.7	SH/T 0509
Asphaltenes (As, %)	7.1	6.9	10.3	10.4	15.8	15.3	SH/T 0509

## 3. Results and discussions

### 3.1. Conventional properties

Table 2 shows that the softening point and ductility at 5 °C for MBERs decrease with respect to their CMBs. The elastic recovery percentage, on the other hand displays relatively uniform values for MBERs. The MBERs, therefore exhibit less resistance to cracking and permanent deformation as well as lower elastic recovery (relative to CMBs). However, with respect to the base bitumens, softening point and ductility at 5 °C for MBERs increase substantially, indicating that the MBERs display improved high- and low- temperature performance.

For each CMB, its MBER demonstrates higher temperature susceptibility in accordance with decreasing PI value. Nevertheless, its PI value is larger than its base bitumen; suggesting improved temperature performance for MBERs.

The storage stability value determined from the difference of softening point of samples obtained from the top and bottom of cylindrical mold indicates that the difference of softening point for each MBER was larger than its CMB. However, the storage stability of all samples does not exceed 2.5 °C; denoting the fact that the MBERs present reasonably good thermal storage properties.

The four fractions of CMBs listed in Table 2 are not affected to a substantial extent by the emulsification as evidenced by their low repeatability error (1.2%, 1.6%, 1.6% and 0.5% for saturates, aromatics, resins and asphaltenes, respectively) and reproducibility error (4.0%, 2.4%, 4.3% and 1.2% for saturates, aromatics, resins and asphaltenes, respectively).

### 3.2. Influence on thermal characteristics

The DSC plots of three CMBs and MBERs are displayed in Figs. 1–3. The absorbed heat (calculated from the peak area) and the glass transition temperature ( $T_g$ ) (obtained from DSC plots) are listed in Table 3. The absorbed heat at different temperature range is different for each CMB and its MBER. As a general trend, the total absorbed heat and  $T_g$  at low temperature for CMBs increase after emulsification which indicates that there is a reduction in thermo-stability. Still,  $T_g$  at low temperature arises from the maltene phase (saturates and aromatics) and it is the most intense transition [16]. For  $M_{CR}$  and  $M_{SR}$ , it shows the total content of saturates and aromatics decreases relative to their CMBs, in agreement with the increase of  $T_g$ . Compared with  $M_Z$ , total content of saturates and aromatics for  $M_{ZR}$  changes slightly consistent with the change of  $T_g$  from 14.6 °C to 14.4 °C. On the other hand, the total absorbed heat only changes slightly for example from 2.469  $\text{J g}^{-1}$  to 2.540  $\text{J g}^{-1}$  (in the case of  $M_C$  and  $M_{CR}$ ). This would mean that the emulsification exerts very little effect on the thermal property of modified bitumen.

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