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Full Length Article

Preparation of a novel flow improver and its viscosity-reducing effect on bitumen

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HIGHLIGHTS

- A novel flow improver materials were successfully prepared.
- The composition of the flow improver is the OASA copolymer.
- OASA modification mechanism was the polar moiety and long alkyl chain.
- The viscosity-reducing effect of OASA was proved.
- OASA has good thermal stability enough to capable for asphalt mixing and compaction.

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ABSTRACT

A novel flow improver, the copolymer of octadecyl acrylate, styrene, and maleic anhydride (OASA), was prepared by copolymerization and esterification reaction to study its viscosity-reducing effect on bitumen based its existing application on crude oil. In this paper, chemical compositions, thermal stability, and viscosity were characterized by infrared spectra (IR), differential scanning calorimetry (DSC), and Brookfield Viscometer, respectively. Besides, conventional properties of modified bitumen were investigated to study the effect of modifier. Results shown that OASA modification was physical and its mechanism was the combination effect of polar moiety and long alkyl chain of OASA copolymer; thermal stability of modifier was good enough to capable for asphalt mixing and compaction; viscosity-reducing effect of OASA was proved with a considerable range and the effect was negative to temperature increasing; as for bitumen conventional properties, penetration and ductility got increased while the softening point got decreased under the OASA modifying effect.

1. Introduction

Recently, warm mix asphalt (WMA) technologies got largely developed due to the benefits such as reducing fuel usage, emissions, and worker exposure [1]. Foaming processes, organic (wax) additives, and chemical additives are three types of most widely used WMA technologies nowadays [2–4]. For current WMA technologies, reducing mix temperature mainly depend on controlling viscosity of asphalt binder via various approaches [5]. Decrease in viscosity can be regarded as the essence of WMA technologies, which enables aggregates to be fully-coated at lower temperature [6]. Therefore, an emerging WMA additive is usually accompanied with new methods of lowering viscosity and the focus of searching a novel additive are usually around flow improvers. Since 1970s, some oil-soluble chemical additives based on esters of styrene maleic anhydride copolymer have been reported as an effective flow improver and pour point depressant for waxy crude oil [7–11]. The mechanism of reducing viscosity of crude oil is based on the mutual action of polar moiety and alkyl chain of polymeric additives [12]. On the one side, the polar moiety such as anhydride can form the stronger hydrogen bonds with polar groups of asphaltene and resin molecules by breaking the original hydrogen-bonding [13]. On the other side, it is the long alkyl chain that stretch and form solvable layer which inhibit re-aggregation of asphaltene and resin molecules. Comparing with the original planar stacking condition, asphaltene-resin aggregation molecules are heaped up irregularly with the looser structure, lower degree of space extension, and lower degree of order under combination effect, which attribute to the significant decrease in viscosity of crude oil [14]. Besides, polymeric additives and derivatives have been furtherly found as effective flow improver for lubricant oil, the heavy refinery products [15].

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Table 1
Physiochemical properties of Karamay 70# bitumen.

Properties of Karamay 70# bitumen	Values
Penetration 0.1 mm, @25 °C	69
Softening point/°C	51.4
Ductility @5 °C, cm	7.8
Penetration index (PI)	−1.8589
Gyration viscosity @135 °C, centipoise	630
Density @15 °C, g/cm^3	1.032
Wax content	1.72

As the residuum of oil fraction distillation, the bitumen is similar with crude oil in component fractions while the contents of asphaltene and resin are higher, which appears the higher viscosity than crude oil [16]. Since the mechanism of the polymeric additives mentioned above is based on breaking coherence within asphaltene and resin molecules, furthermore, there are merely previous research of this polymeric additives effect on bitumen, it is significant and deserving to apply the esters of styrene maleic anhydride copolymer to bitumen and evaluate the effect on reducing viscosity and basic properties.

On the basis of previous preliminary work, in this paper, copolymer of octadecyl acrylate, styrene, and maleic anhydride (OASA) was chosen as flow improver. Preparation of OASA comprised the esterification and copolymerization reactions [17]. Morphology characteristics of OASA were investigated by infrared spectra test (IR) and thermal analysis was conducted by differential scanning calorimetry test (DSC). The variation of apparent viscosity was measured by Brookfield Viscometer. The experiments of penetration, softening point and ductility of bitumen were committed to evaluate the effect of OASA addition.

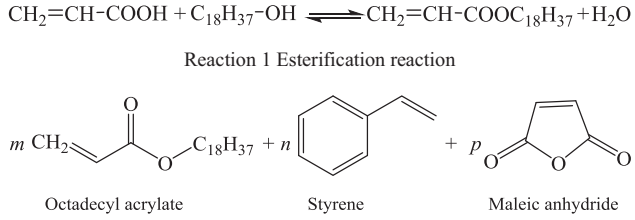
2. Experimental

2.1. Materials

Raw materials included octadecanol, acrylic acid, p-toluene sulfonic acid (PTSA), toluene, hydroquinone, Benzoyl peroxide (BPO), maleic anhydride (MA), and styrene (ST) were purchased as analytical grade. Virgin bitumen was produced from Karamay (Xinjiang, China) and basic properties were listed in Table 1.

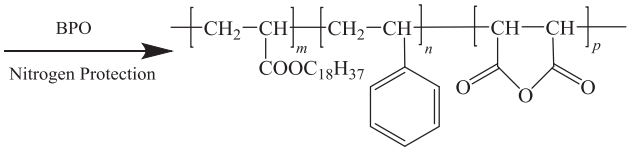
2.2. Esterification and copolymerization reactions

The mono-esters, octadecyl acrylate (OA), was individually prepared via esterification reaction between octadecanol and acrylic acid. Molar feed ratio of octadecanol and acrylic acid was 1.2:1, reaction time was controlled as 6 h, and reaction temperature was set as 120 °C. PTSA served as catalyst and its dosage was 1.0 wt%. Hydroquinone was applied as inhibitor with the dosage as 0.6 wt%. Besides, toluene served as water-carrying agent and its dosage was determined as 40 ml. OASA was prepared by copolymerizing octadecyl acrylate, styrene, and maleic anhydride. Molar feed ratio of OA:ST:MA varied from 5:1:3 to 5:3:5. Reaction time was controlled as 6 h and reaction temperature was fixed as 80 °C. BPO served as initiator with the dosage as 1.0 wt%. The details of esterification and polymerization were referenced to the procedures described by Song and Guan [18,19]. The equations of esterification and polymerization reactions were listed as follows:



Reaction 1 Esterification reaction

Octadecyl acrylate Styrene Maleic anhydride



Copolymer of octadecyl acrylate, styrene, and maleic anhydride

Reaction 2 Copolymerization reaction

2.3. Preparation of OASA-modified bitumen

While preparing OASA-modified bitumen, virgin bitumen was firstly heated above 130 °C and then blended with the OASA addition. Molar feed ratio of OA:ST:MA varied from 5:1:3 to 5:3:5. The dosage of modifier was varied from 3% to 7%. Process of adding OASA should be slowly and kept uniformed. The blending was committed by electric blender. Mixing velocity ranged from 450 r/min to 600 r/min and stirring time was determined as 15 min.

2.4. The FT-IR analysis of bitumen and OASA additives

The compositions of virgin bitumen, OASA-modified bitumen, and the OASA additives were investigated by IR spectra test. Specimens for IR test included virgin bitumen, copolymer OASA with four different molar feed ratios (OA:ST:MA were 5:1:5, 5:2:5, 5:3:3, and 5:3:4), and OASA-modified bitumen whose molar feed ratios were mentioned above. IR spectra test were conducted on each specimen with the dosage as 5%, respectively. The test method was KBr pellet technique and acetone was solvent.

2.5. The thermal analysis of OASA additives

The thermal analysis of OASA was conducted by DSC test. Specimen for DSC test were two different copolymers which were designated as OASA1 and OASA2 for OA:ST:MA molar feed ratios were 5:2:5 and 5:3:4, respectively. The amount of OASA1 and OASA2 specimen were taken as 11.33 mg and 11.03 mg. For experimental settings, heating rate was fixed as 10 °C/min, velocity of Nitrogen flow was set as 30 ml/min, initial measuring temperature was −40 °C, and ending measuring temperature was 200 °C.

2.6. Measurements of apparent viscosity

Brookfield DV-II+ viscometer was utilized to measure apparent viscosity of virgin bitumen and OASA-modified bitumen with the dosage of modifier addition as 3%, 4%, 5%, 6% and 7%. With consideration viscosity reduction effect of OASA additives, both virgin bitumen and OASA-modified bitumen were adopted as S21# rotor. Reaction temperature ranged from 110 °C to 160 °C.

2.7. Evaluation of bitumen conventional properties

Technical properties included penetration, softening point, and ductility was evaluated for both virgin bitumen and OASA-