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Characterization of asphaltenic material obtained by treating of vacuum residue with different reactive molecules

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HIGHLIGHTS

- Modification and separation of asphaltene from natural bitumen have been discussed.
- How the asphaltenes are formed and how it changes the final properties of modified bitumen have been highlighted.
- Modified asphaltenes have been characterized in details.

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ABSTRACT

Natural bitumen which is generally used for highway paving has a short life cycle, due to traffic load and drastic change of pressure and temperature. To get the appropriate physical properties of this bitumen, it is generally modified by using reactive molecules. In this study, glycerol, styrene, methyl methacrylate (MMA), hydroquinone (HQ), and C18 acrylate molecules are used as modifiers. The required amounts of the modifier and bitumen are heated at 200 °C for 8 h with continuous stirring. The asphaltene is extracted from these modified bitumen by soxhlet process. The physical properties of the dried asphaltene are characterized by XRD, SEM and TGA. Results show that the hardness properties, like penetration, softening point, ductility of the natural bitumen are substantially improved after treatment with the modifiers. XRD results indicate that asphaltenes extracted from the modified bitumens become more compact than the asphaltene from the natural bitumen. The results also show that the number of aromatic sheets increases due to the treatment of natural bitumen with the modifiers. The asphaltene derived from C18-acrylate modified bitumen has the maximum number of aromatic sheets. The presence of vinyl double bond and –COOR functional group in C18-acrylate helps effectively the polymerization reaction between the modifier and the natural bitumen. SEM and TGA results also support the presence of a high degree of polymerization/structural arrangement in the asphaltene obtained from this modified bitumen.

1. Introduction

Natural bitumen is mainly used for highway paving. However, this base bitumen obtained directly from refinery does not have sufficient strength to withstand sudden stress of excessive loading or stress from low temperature during winter. This bitumen should also be hard enough so that it should not deform at high temperature. To get these properties of the natural bitumen several modifiers or binders are used. It is found in the literature, that air blowing was industrially used for the modification of soft bitumen for hardening. However, it was later found that air blowing increased fragility of the binders as well as higher aging susceptibility which was not good for paving purposes [1–3]. Rheological modification of a bitumen with maleic anhydride and dicarboxylic acids was studied by Herrington et al. [4]. It was found that the visco-elastic property of the bitumen changed at lower concentration of the modifiers. It was proposed that this change mainly took place due to the formation of transient networks of bitumen species, linked by hydrogen bonding and dipole–dipole interactions.

The aggregation of asphaltenes has been studied by *in situ* with small angle neutron scattering [5]. Maya, Khafji and Iranian light were used for the different sources of the asphaltene. Around 5 wt% of asphaltene obtained from these sources was mixed with different solvent like decalin, 1-methylnaphthalene and quinoline. The shape and size of these asphaltene aggregates at various temperatures were investigated. It was noted that the size and shape of asphaltene-aggregates changed depending on the source, solvent

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Nomenclature

A	asphaltene	D27	ductility at 27 °C
B	bitumen	Kv	kinematic viscosity
N	natural	M_{wt}	molecular weight
g	glycerol ($CH_2OHCHOHCH_2OH$)	FT	fail temperature
s	styrene ($C_6H_5CH{=}CH_2$)	*dm*	layer distance between aromatic sheets
mma	methyl methacrylate ($CH_2{=}C(CH_3)COOCH_3$)	$d\gamma$	interchain layer distance
hq	hydroquinone ($C_6H_4(OH)_2$)	*Lc*	average height of stack aromatic sheets
acl	C18-acrylate ($C_{21}H_{40}O_2$)	*M*	molecules of aromatic sheets in a stacked cluster
A_n	asphaltene derived from natural bitumen	G'	storage modulus
B_n	natural bitumen	G''	loss modulus
Ins	insoluble	G^*	complex modulus
P25	penetration at 25 °C	δ	phase angle

and temperature. Maya asphaltene in decalin solvent forms a fractal network and this network sustains at high temperature like 350 °C, indicating the high coking tendency of Maya crude. Due to the presence of high aromaticity, the Iranian light asphaltene precipitates comprehensively in decline even at lower temperature. In their other studies, Tanaka et al. [6] reported a three main hypothetical aggression of asphaltene as (i) core aggregates are formed by π–π stacking of asphaltene molecules (20 Å size), (ii) medium aggregates are formed by secondary aggregation of core aggregates that result from interactions with maltenes, oils or solvents (50–500 Å) and (iii) fractal aggregates are secondary aggregates of core aggregates that results from diffusion limited cluster aggregation or reaction limited cluster aggregation (which is independent of any media) (size > 1000 Å). It was also concluded by the authors that this model of asphaltene aggregate was a highly simplified model. The usefulness of other recycled waste materials like glass, steel slag, tyres, rubbers and plastics for bitumen pavements has been discussed in detail in the literature [7–11].

Regardless of the chemical used, the reaction conditions and sources of a bitumen, the modification increases asphaltene content in the bitumen cluster and hence the soft property of the bitumen becomes hard. The degree of hardening depends on several factors like-source of bitumen, chemical use and reaction conditions, etc. Although several research work are found in the literature for modification of a bitumen by chemical reaction, still the formation of asphaltenic material and its nature are so complex, that there is no clear explanation of how asphaltenes are formed and how it changes the rheology of the bitumen. But it is proved as stated above that the presence of asphaltene molecules in the bitumen improves significantly its properties and hence it can be used for paving or other purposes. Therefore, in this study, different bitumen modifiers are used and the effects of these modifiers on asphaltene's properties are examined. For these reasons, glycerol, styrene, methyl methacrylate (MMA), hydroquinone (HQ) and C18-acrylate are used as modifiers. The asphaltenes extracted from these modified bitumen are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and thermogravimetric analysis (TGA).

2. Experimental

2.1. Modification of bitumen and asphaltene separation

Vacuum residue (VR, 540 °C+) procured from the Indian refinery (Panipat) was used as a base material (bitumen). Around 200 g of the base material was heated into a flask with continuous mechanical stirring. After getting desired temperature, the required quantity of modifier was added and the mixture was stirred for a period of 8 h. All chemicals except C18-acrylate were of commercial grade. C18-acrylate was synthesized in our laboratory according to the procedure given elsewhere [12]. Asphaltene was extracted from the modified bitumen by soxhlet process. In this process the modified bitumen was taken with n-heptane (ten times of bitumen) solvent into a round bottle. The mixture was then refluxed for a period of 6 h. The insoluble portion was separated and dried in a vacuum oven at 110 °C. A flow diagram of the separation of asphaltene is presented in Fig. 1.

2.2. Characterization of modified bitumens and asphaltenes

The physical properties like-penetration, ductility, softening point of the untreated and treated bitumens were measured by standard methods. The penetration is determined by a standard method (ASTM D5) with a penetrometer. In this method, a needle loaded with 100 g was brought to the sample surface at right angle, allowed to penetrate the sample for 5 s at 25 °C. The penetration is measured in deci-millimeter (dmm). The ductility of a sample is measured by ASTM D113 method. In this method a sample was pulled apart at a uniform rate of 5 cm/min. at 27 °C until it ruptured. The elongation or stretch of the sample in centimeter was measured. The softening point was determined by ASTM D 36 method by using ring and ball apparatus. The average molecular weight of the natural and modified bitumen were also measured by Agilent Gel Permeation Chromatography (GPC) using model 1260.

The dynamic shear rheometer of TA instrument of model AR 1500eX was used to characterize visco-elastic behavior of natural and modified bitumens. Rheological study was carried out at minimum instrument inertia of 16.85 μN m^2 as per ASTM D7175-05. Different rheological parameters like G^*, δ, $G^*/\text{Sin}\,\delta$ at 1.1 kPa gives the fail temperature. It is the temperature at which bituminous

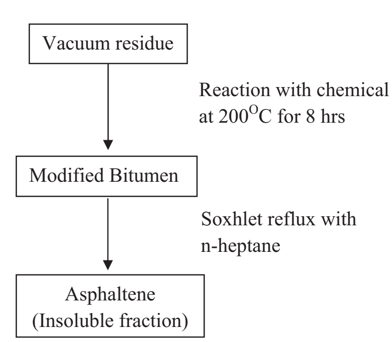

Fig. 1. Separation of asphaltenes from vacuum residue.