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Effect of nanoclay on the morphology of polyethylene modified bitumen

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HIGHLIGHTS

- Effect of clay on phase morphology of polyethylene modified bitumen was studied.
- The clay dispersion was dependent on the content and functionality of polyethylene.
- The order of mixing influentially affected the phase morphology of polymeric phase.
- The melting temperature of polyethylene phase in bitumen was decreased.

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ABSTRACT

The main objective of the present work was to study the effect of nanoclay on the morphology of polyethylene modified bitumen. The bitumen was modified simultaneously with polyethylene and/or maleic anhydride grafted polyethylene and nanoclay in a high shear mixer and characterized by means of morphology and clay dispersion state. The results showed that the state of nanoclay intercalation and/or exfoliation strongly depends on the polymeric phase content, functionality of polyethylene and the mixing procedure of the components. In turn, the dispersion state of the nanoclay influentially affected the phase morphology of swelled polymeric phase. Using functionalized polyethylene and premixing of nanoclay with polyethylene phase led to improved dispersion state of nanoclay in bitumen nanocomposites. Absorption of low molecular bituminous fractions, led to decreased melting temperature of polymeric phase. The presence of nanoclay induced phase separation between polyethylene and functional polyethylene due to higher affinity of nanoclay to functional polyethylene.

1. Introduction

Bitumen has widely been used as a binder of aggregates in the construction of asphalt due to its useful viscoelastic properties. However, increased traffic loads combined with variation of weather conditions reduce the performance of asphalt [1–4]. On the other hand, temperature sensitivity of bitumen intensifies deterioration of pavements. Bitumen should be stiff enough at high temperatures to resist against rutting and it must remain soft enough at low temperatures to prevent cracking phenomenon [5]. These properties are quite opposite and the final goal of bitumen modification is to overcome upcoming problems.

Several modifiers such as carbon black and sulfur have been applied to improve the properties of bitumen, but they were not useful and then remained despicable [6]. In last decades, polymer modified bitumen (PMB) has extensively been used as a promising alternative to alleviate pavement defects [7–12]. Among the used polymers, styrene-butadiene-styrene (SBS) rubber, ethylene-vinyl acetate (EVA) copolymer and polyethylene (PE) have presented acceptable effects on modification of bitumen but they still have not shown perfect performance to employ in pavements [13–16]. Also, reactive polymers such as thermoplastic elastomers functionalized with maleic anhydride and ethylene-based copolymers containing epoxy rings have recently been employed in modification of bitumen [21]. Chemical stabilization of reactive polymers within the bitumen takes place when the polymer chains interact, yielding the formation of chemical interactions [22].

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Polyethylene based modified bitumen is less expensive and shows more resistance to UV aging and rutting [4,17,18]. Previous studies have reported that addition of PE significantly improves the rheological properties of bitumen [10,19,20]. Influence of PE concentration on the morphology and rheology of modified bitumen was investigated by Pérez-Lepe et al. [10]. It was shown that addition of PE to bitumen enhances the mechanical properties of the binders, especially at high temperature region, where pavements can be submitted to permanent deformations. Although polymer modified bitumen exhibits much more elastic behavior, it undergoes phase separation during the mixing processes and particularly at the storage conditions due to the difference in density of its various components [2,22]. Thus, the key point in polymer modification of the bitumen is the formation of a stable morphology [23].

In recent years various nanofillers have been used in bitumen modification processes [24–27]. Layered silicates have been used as a surfactant to interconnect different phases in bitumen and/or polymer modified bitumen. Infiltration of polymer chains into the interlayer of nanoclay platelets (intercalation), leads to significant improvement on dispersion and distribution of nanolayers in bitumen nanocomposites [3]. It is anticipated that montmorillonite with large aspect ratio will enhance the morphology stability of polymer modified bitumen [3,4]. The effect of nanoclay on the properties of polymer modified bitumen was studied by Polacco et al. [12]. It was shown that the clay had a compatibilizing effect on bitumen and polymer. When the clay had more interaction with polymer, it led to a better dispersion that affected the morphology and rheological properties.

It is generally assumed that bitumen has a complex colloidal structure in which the asphaltenes are dispersed in other low molecular weight components (maltenes). In polymer modified bitumen, polymer phase absorbs maltene fractions to form swollen regions [28]. Ternary nanocomposite of bitumen/polymer/nanoclay is a novel approach to bitumen modification. Polymer and nanoclay cooperate to have effective interactions into bitumen [2,3,7]. If the nanofillers localize at the interface of these two different phases, it would improve the morphology and hence storage stability. Mixing procedure would also be important to gain the desired morphology. Compatibility between polymer and bitumen is related to microstructure of polymer and bitumen. It is expected that nanoclay and functional polymers will improve the interactions between polymer and bitumen and so that the obtained morphology could be more stable. Improvement of bitumen properties is an outcome of microscopic changes in the morphology of the blend.

The main objective of this work was to study the morphology of PE modified bitumen and the influence of nanoclay and reactive functional polymer (maleic anhydride grafted polyethylene; PE-g-MA) on its morphology. PE-g-MA was chosen because of its twofold characteristic. Maleic anhydride groups would interconnect polymer chains to polar asphaltenic groups whilst the backbone of the polymer chain is constituted by non-polar hydrocarbons. The effect of mixing procedure on the shapes and distribution of phases was also examined.

2. Experimental

2.1. Materials

An 85/100 penetration grade bitumen was provided by Pasargad Company, Tehran, Iran. Physical properties and chemical compositions of the base bitumen are listed in Table 1. The bitumen was modified with pelletized high density polyethylene (HDPE-5218; MFI = 18, 190 °C, 2.16 kg) supplied by Tabriz Petrochemical Company, Iran. Maleic anhydride grafted polyethylene (PE-g-MA) was obtained from Pluss Polymers Company, India (E-142; MFI = 2.0 g/10 min; 2.16 kg, 190 °C; degree of grafting = 1.0 wt%). The used nanoclay was Cloisite 20A obtained from Southern Clay Products, USA. It is an organophilic sodium montmorillonite having a cation exchange capacity of 0.926 meq/g by treatment with 2M2HT (dimethyl, dehydrogenated tallow, quaternary ammonium).

Table 1
Physical properties and chemical compositions of the used base bitumen.

Properties	Results	Compositions	Results
Viscosity at 160 °C (Pa s)	0.087	Saturates (wt%)	13.5
Penetration at 25 °C (0.1 mm)	98	Aromatics (wt%)	41.2
Softening point (°C)	46	Resins (wt%)	34.8
Ductility at 15 °C (cm)	+100	Asphaltenes (wt%)	10.5

2.2. Preparation of the samples

The composition and related codes of different prepared samples are listed in Table 2. All of the samples were prepared in a high shear mixer at 180 °C with a rotation speed of 5500 rpm. The organoclay was dried in a vacuum oven at 80 °C for 12 h prior to mixing. Two different methods were used for blending of polyethylene phase (HDPE and/or PE-g-MA) and nanoclay with bitumen. In the physical mixing method (PM), nanoclay was added into bitumen and mixed for 15 min at first and then polyethylene phase was added to the mixture and further mixed for 30 min and the prepared samples were marked 'PM' samples. In the second method, the nanoclay was first compounded with polyethylene phase in an internal mixer (Brabender, W50 EHT) for 10 min at starting temperature of 170 °C with a rotor speed of 60 rpm. The obtained masterbatches were cut into small pieces and then added to the hot bitumen in high shear mixer and the mixture was sheared for 45 min and resulted mixtures were named 'MB' samples. Bitumen/polyethylene phase and bitumen/clay mixtures as reference samples were also prepared using the same procedures. Finally, all the samples were molded into suitable forms for different tests. They were stored at −18 °C immediately after their preparation to avoid polymer-bitumen phase separation.

2.3. Characterization

X-ray diffractometry technique (XRD) was used for evaluation of the clay dispersion and its interlayer distance in the different mixtures. The XRD spectra were obtained using X'pert-Philips diffractometer with CuKa radiation (k = 1.54 A°, 40 kV, 30 mA) at room temperature. Scanning was done from 2θ range of 1°–10° with the scanning rate of 2°/min.

Morphological characterization was performed using an optical microscopy equipped with a hot-stage. A small amount of the modified bitumen samples was inserted between two quartz lamellas on the hot-stage at the fixed temperature of 163 °C. Then the images were taken by optical microscope.

The thermal behavior of the samples was studied using differential scanning calorimetry (DSC) technique with Netzsch-DSC 20 0F3 (Germany) instrument under nitrogen atmosphere.

3. Results and discussion

3.1. XRD spectroscopy

The dispersion state of nanoclay and its interlayer distance in different samples were investigated by XRD technique. If the

Table 2
The composition and related codes of different prepared samples.

Sample	Bitumen (wt%)	HDPE (wt%)	Cloisite 20A (wt%)	PE-g-MA (wt%)	Mixing method
Base bitumen	100	0	0	0	–
N1	99	0	1	0	–
H2	98	2	0	0	–
H2N0.5	97.5	2	0.5	0	PM
H2N1	97	2	1	0	PM
H4	96	4	0	0	–
H4N1	95	4	1	0	PM
H4N2	94	4	2	0	PM
MB1	94	4	2	0	MB
H6	94	6	0	0	–
H6N1.5	92.5	6	1.5	0	PM
H6N3	91	6	3	0	PM
G4	96	0	0	4	–
G4N2	94	0	2	4	PM
MB2	94	0	2	4	MB
HG4	96	2	0	2	–
HG4N2	94	2	2	2	PM
MB3	94	2	2	2	MB