Preparation and rheological characterization of asphalt binders reinforced with layered silicate nanoparticles

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Abstract

Bentonite clay (BT) and organically modified bentonite (OBT) were used to reinforce and modify a bituminous paving asphalt binder. The modified asphalt binders were produced by melt processing under sonication and shearing stresses. The interlayer spacing of silicate layers in bentonite, organically modified bentonite and the modified asphalt binders were analyzed by wide angle X-ray diffraction (WAXD). The softening point, viscosity and ductility of the modified asphalts were tested as a function of clay content and clay type. The dynamic shear rheological tests showed that the modified asphalts have higher rutting resistance. Bending beam rheometer (BBR) test results for aged specimens (through rolling thin film oven (RTFO) and pressure aging vessel (PAV)) indicated that adding BT and OBT can significantly improve low temperature rheological properties and cracking of asphalt.

Keywords: Asphalt binder; Bentonite; Layered Silicates; Nanocomposites.

1. Introduction

Asphalt (or bitumen) is used in road pavements as the binder of aggregates in a great extent all around the world. Asphalt pavements must undergo heavy loads and unfavorable environmental conditions for an acceptable period of time. High-temperature rutting and low temperature cracking are the most considerable limitations of unmodified and pure asphalts [1]. Therefore, modification and reinforcement of asphalt binder is necessary.

Asphalt usually is a byproduct of crude oil refining process in petroleum refineries, and it is a complex heterogeneous mixture of hydrocarbons [2].

The first studies on the use of nanoclay or layered silicate nanoparticles as filler and reinforcing agent were reported by Toyota’s researchers with the production of nylon 6/clay Nanocomposites [3,4]. Polymer/layered silicate nanocomposites have showed significantly enhanced mechanical [5], thermal [6] and barrier [7] properties compared to the pure polymer matrix with addition of a minimal amount of filler. Therefore, various types of polymers (such as addition polymers [8-10], condensation polymers [11-13] and biodegradable polymers [14, 15]) have been studied and used as the matrix in these nanocomposites.

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The dispersion of clay particles in the matrix can form three types of structures (Fig. 1). The first one is the conventional composites structure in which the silicate platelets are agglomerated. The second one is intercalated nanocomposites structure, where some matrix molecules are inserted between individual silicate layers, but the layers remain parallel. The third type is the exfoliated nanocomposites structure, in which the layered structure of the clay is disrupted, with the silicate layers no longer close enough to interact with each other and nanometric particles are fully dispersed in the matrix [16]. Typical clays capable of forming intercalated or exfoliated structures include montmorillonite, fluorohectorite and bentonite [17].

In order to obtain a good interfacial adhesion and mechanical properties, the hydrophilic clay needs to be modified prior to introduction in most polymeric matrices that are organophilic. Clay modification is generally achieved by ion exchange reactions of organophilic cations by sodium ions which are naturally between the clay layers [18]. Clay-containing nanocomposites may be obtained mainly by three methods: in-situ polymerization [19-21], solution blending [22-24] and melt processing [25-27].

Yu and coworkers [28] have used montmorillonite (MMT) clay and organically modified montmorillonite (OMMT) to modify asphalt. They have investigated the physical properties, dynamic rheological behaviors and the high temperature storage stability of the modified asphalts. They showed that the MMT and OMMT modified asphalts have higher rutting resistance and very good storage stability. Also, in a recent work, the effect of OMMT on thermo-oxidative and UV aging properties of asphalt is investigated by Yu et al [29].

In this paper, sodium bentonite (BT) and organically modified sodium bentonite (OBT) are used to reinforce and modify asphalt binder. BT is a sedimentary rock consisting, to a large proportion, of clay minerals with a typical 2:1 layered structure (smectites) and a high concentration in sodium ions [30]. Indeed, BT is a clay mineral which is rich in MMT [31]. BT has natural abundance and low cost which can make it economically more suitable for this purpose. In this research the physical properties and high temperature dynamic rheological behavior of the BT and OBT modified asphalt binders were studied. Also, low temperature cracking properties of the modified asphalt binders were evaluated after artificially short-term and long-term aging.

2. Experimental Methods

2.1. Materials

Asphalt, 60/70 penetration grade bituminous paving asphalt binder was produced in Tehran refinery and supplied by Pasargad Oil Co, Tehran, Iran. The physical properties of the asphalt are listed in Table 1, and its chemical compositions are listed in Table 2. Sodium bentonite clay with cation exchange capacity (CEC) of 110 meq/100 g was supplied by Chavosh Maadan Co, Tehran, Iran. Octadecylamin and HCl were purchased from Merck Co, Germany.

2.2. Clay modification

Before the clay modification, a purification process was performed. The purification process consisted of the following steps: (a) water dispersion of the as received clay and 24 h aging to ensure swelling of clay, (b) elimination of supernatant and sediments. The organically modified bentonite was produced by ion exchange reaction between bentonite and octadecylammonium salt which was obtained after protonation of octadecylamine by adding hydrochloric acid to the reaction medium during the process, before the ion exchange reaction can occur. Thus, octadecylamine was previously
mixed with HCl in water and heated at 80° C for a few minutes. The CEC ratio of ODA/clay was 1.5 and the molar ratio of ODA/HCl was 1:1. The as-protonated surfactant was drop wise added to the clay suspension and maintained at 80° C for 1 h under vigorous stirring. Then the suspension was cooled to room temperature. This suspension was dispersed and washed with water twice. A third dispersion and washing was accomplished using a 50/50 ethanol/water mixture. The final washed modified clay was dried at 75° C by a hot air blower device, and then powdered by a ball mill device. The organically modified bentonite powder was sieved through a 50 μm steel mesh. This method is similar to the method described in reference [18]. However, in this work the solid percent of the clays that is modified during the process has been varied (10% and 20%) and a different clay drying procedure has been used.

2.3. Preparation of modified asphalts
The modified asphalts were prepared at 160 °C. The measured amounts (1, 2, 4, 5, 6 wt%) of BT or OBT were gradually added into 1.5 liter volumes of the base asphalt binder when mixing by a simple mixer in beakers. The mixtures were blended at 4000 rpm rotational speed for about 1 hr using a Silverson-L4RT high shear mixer, and then sonicated with a Missonix sonicator device with 20kHz sound waves for 10 minutes in order to allow the better dispersion of BT or OBT nanoparticles.

2.4. Aging of asphalt binders
Asphalt binders age mainly due to two different mechanisms: (a) volatilization of light oils present in the asphalt, (b) oxidation by reacting with the oxygen in the environment. The blending and agitation in the hot mixing facility and during placement ages the binder by both mechanisms because of the high temperature and air flow involved in the process. The rolling thin film oven (RTFO) procedure is used to simulate this form of aging. After the asphalt pavement is constructed, aging continues, but the oxidation mechanism dominates because of the relatively moderate temperatures of the environment. The pressure aging vessel (PAV) is used to simulate this in-service aging [32].

The base asphalt binder, 5% BT modified asphalt and 5% OBT modified asphalt were artificially short-term and then long-term aged through RTFO aging (ASTM D 2872) and then PAV aging (AASHTO PP1). The aged samples were used in the bending beam rheometer test.

2.5. Characterizations
Wide angle X-ray diffraction (WAXD) of the clays and modified asphalts was performed in a Brucker axs-D8 diffractometer using CuK radiation (λ = 0.154 nm; 40 kV, 30 mA) in order to evaluate the evolution of clay d_{001} reflections. The scanned range was from 1° to 12° in the 2θ with a scanning rate of 1.2° min⁻¹.

The physical properties of the asphalts, including softening point (Strassentest ring and ball Instrument), ductility at 25°C (Strassentest Instrument) and viscosity at 135°C (Bohlin Instrument), were tested according to ASTM D 36, ASTM D 113 and ASTM D 4402, respectively. Each of these tests were performed 3 times for the (0, 1, 2, 4, 6 wt %) BT and OBT modified asphalts and the average values of the results were used.

A Dynamic Shear Rheometer (Bohlin Instrument) was used for dynamic rheological measurements in plate–plate mode (1mm thickness, 25 mm diameter) for base asphalt, 5% BT modified asphalt and 5% OBT modified asphalt according to AASHTO TP5. Temperature sweeps from 46 to 70°C with 6°C increments were applied at a fixed frequency of 10 rad/s and variable strain.
The bending beam rheometer (BBR) test (Cannon Instrument Company) was conducted using aged base asphalt, aged 5% BT modified asphalt and aged 5% OBT modified asphalt beams (125 × 6.35 × 12.7 mm) at -12 °C, and creep stiffness (S) and creep rate (m) of the binders were measured at a loading time of 60 s according to AASHTO TP1.

3. Results and discussion

3.1. WAXD Test results

The interlayer spacing of silicate layers which shows the extent of intercalation or exfoliation of the clay in the asphalt matrix was studied by WAXD technique. The WAXD patterns of BT, OBT, BT modified asphalt and OBT modified asphalt are shown in Fig. 2. The interlayer spacing of clay (d_{001}) has increased from 1.48 nm for BT to 3.16 nm for OBT due to the modification of clay with octadecylammonium. The interlayer spacing of the clay layers in the bentonite modified asphalt is 1.95 nm which shows the intercalation of asphalt molecules into the clay gallery space, therefore the BT modified asphalts may form an intercalated structure. The WAXD pattern of OBT modified asphalt does not show any peak, and we can conclude that the clay layers are dispersed in the asphalt, and are not close enough together to be able to create peaks in the WAXD pattern. It means that the OBT modified asphalts may form an exfoliated structure.

3.2. Properties of the modified asphalts

The relationship between the modified asphalt binders softening point and the BT and OBT contents is represented in Fig. 3a. The addition of BT and OBT leads to improvement in the softening point of the modified asphalt binders, and OBT has greater effects than BT.

The viscosity of the modified asphalt binders as a function of clay content is shown in Fig. 3b. Viscosity increases with the increase of filler loading. This is due to the addition of the solid phase of clay to the viscous phase of asphalt. OBT increases viscosity more than BT; This may be related to the exfoliated structure in the OBT modified asphalts which has a better dispersion of clay layers than the intercalated structure in the BT modified asphalts.

The ductility of the asphalt binders decreases when the amount of BT and OBT increases (Fig. 3c). This is due to the addition of solid brittle phase of clay to the ductile viscoelastic phase of asphalt. On the other hand, BT modified asphalt shows a greater decrease in ductility than OBT modified asphalt, because OBT nanoparticles have better dispersion in asphalt and they are more consistent with the organic composition of asphalt due to its surface modification by octadecylammonium.

The variations of complex modulus ($G^*$) against temperature for the BT and OBT modified asphalts are depicted in Fig. 4a. The complex modulus consists of elastic modulus and viscous modulus. $G^*$ increases by the addition of OBT and BT to asphalt (Fig. 4a).

The OBT modified asphalts exhibit higher complex modulus relative to BT modified asphalts. It may be related to the exfoliated structure of OBT in asphalt.

The variations of phase angles ($\delta$) against temperature for the BT and OBT modified asphalts are depicted in Fig. 4b. Phase angle is defined as the phase difference between stress and strain in an oscillatory test. A greater $\delta$ value shows a more viscous behavior and a smaller $\delta$ shows a more elastic one. The phase angles of the binders decreases with addition of BT and OBT. Therefore, the elastic behavior of asphalt increases with addition BT and OBT. Moreover, the OBT modified asphalts show lower phase angle
than the BT modified asphalts, which may be due to exfoliated structure of OBT modified asphalts.

The strategic highway research program (SHRP) rutting parameter ($G*/\sin(\delta)$) for the base and modified asphalts is represented in Fig. 4c. This parameter shows the binder resistance to permanent deformation and rutting. The rutting parameter should be larger than 1 kPa for the binder at a maximum pavement design temperature. The maximum temperature in which the binders satisfy the criterion ($G*/\sin(\delta) > 1kPa$) is increased from 65.3ºC for the base asphalt to 67.2ºC for 5% BT modified asphalt and 67.9ºC for 5% OBT modified asphalt (Fig. 4c).

From the BBR tests at -12 ºC, the creep stiffness and the m-value (the rate at which binder stiffness changes with time at low temperatures) for the base and modified asphalts after RTFO + PAV aging were calculated, and the results are represented in Fig. 5. Superpave asphalt binder specification includes a maximum value of 300 MPa for creep stiffness and a minimum m-value of 0.300, and the decrease in creep stiffness is expected to lead to smaller tensile stresses in the asphalt binder and less chance for low temperature cracking [32]. The results indicated that the BT and OBT modified asphalts yielded lower stiffness than the base asphalt, indicating that the addition of BT and OBT result in the binder being more resistant to low temperature cracking. The OBT modified asphalt showed the lowest stiffness and the highest resistance to low temperature cracking. The BT modified asphalt showed the highest m-value but, the OBT modified asphalt exhibited a lower m-value than the base asphalt.

The lower creep stiffness of aged BT and OBT modified asphalts relative to the base asphalt binder shows that clay platelets in the asphalt matrix prevent oxidation of the matrix molecules and volatilization of light oil molecules from the matrix. As can be seen in Fig. 6, the path of the influx of oxygen and the path of exit of light oil molecules become more distant with the introduction of clay platelets in the asphalt matrix. The movement of gas molecules in the exfoliated structure of OBT modified asphalt is more difficult than the intercalated structure of BT modified asphalt (Fig. 6). As a result, OBT modified asphalt showed the lowest creep stiffness in the BBR test and highest resistance to aging (Fig. 5a).

4. Conclusion

The bentonite and organically modified bentonite were used to reinforce and modify asphalt binder by melt processing under sonication and shearing stresses. The structures of the modified asphalts were studied with WAXD technique. An intercalated structure was suggested for BT modified asphalt, whereas the suggested structure for OBT modified asphalt is exfoliated.

The BT and OBT modified asphalts have shown greater softening point and viscosity than the base asphalt. But the ductility of the modified asphalts decreased with the addition of BT and OBT. The BT and OBT modified asphalts have shown better dynamic rheological properties than the base asphalt. The modified asphalts exhibited higher complex modulus, lower phase angle and higher rutting parameter. Therefore, the rutting resistance of the modified asphalts was improved.

The BT and OBT modified asphalts were observed to have significantly lower creep stiffness in the BBR test. Therefore, the low temperature cracking resistance was improved by addition of BT and OBT.

The OBT modified asphalts has better properties than the BT modified asphalts which may be related to: (a) The exfoliated structure of the OBT modified asphalts which has
a better dispersion of clay platelets in the matrix, (b) the better surface compatibility of OBT nanoparticles with the organic molecules of the asphalt matrix.

References


Figures:

Figure 1: Schematic illustrations of possible structures for the dispersion of clay particles in a matrix: Conventional composites, Intercalated nanocomposites and Exfoliated nanocomposites.

Figure 2: Wide angle X-ray diffraction patterns of bentonite (BT), organically modified bentonite (OBT), BT modified asphalt and OBT modified asphalt.
Figure 3: (a) Softening point (b) Viscosity (c) Ductility of the BT and OBT modified asphalts.
Figure 4: (a) Complex shear modulus $G^*$ (b) Phase angle $\delta$ (c) SHRP rutting parameter $G^*/\sin \delta$ against temperature for the base and modified asphalts.
Figure 5: (a) Stiffness and (b) m-value at -12 °C for the base and modified asphalts after RTFO + PAV aging.
Figure 6: Schematic illustrations of path of the influx or exit of gas molecules: A comparison between permeability of the pure asphalt, BT modified asphalts and OBT modified asphalts.
Table 1.  
Conventional physical properties of the base asphalt

<table>
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<tr>
<th>Binder Type</th>
<th>Penetration at 25°C (dmm)</th>
<th>Softening point (°C)</th>
<th>Viscosity at 135°C (Pa.s)</th>
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<tr>
<td>60/70</td>
<td>61</td>
<td>50.1</td>
<td>0.451</td>
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Table 2.  
Chemical composition of the base asphalt

<table>
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<th>Binder Type</th>
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<th>Resins (%)</th>
<th>Saturates (%)</th>
<th>Aromatics (%)</th>
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<td>60/70</td>
<td>12.2</td>
<td>30.8</td>
<td>8.1</td>
<td>48.9</td>
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