This is an Accepted Manuscript of an article published by Taylor & Francis in Road Materials and Pavement Design on 27 Apr 2018 (published online), available at: http://www.tandfonline.com/10.1080/14680629.2018.1465842.

Improvement of storage stability of SBS modified asphalt with nanoclay using a new mixing method

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Storage stability at high temperature is one of major concerns of styrene-butadiene-styrene (SBS) modified asphalt. This study aims to address this concern by incorporating nanoclay into SBS modified asphalt. To achieve this objective, SBS-nanoclay modified asphalt were prepared with three types of nanoclay and two mixing methods, i.e., directly mixing SBS, nanoclay and base asphalt binder together (direct mixing or DM) and fabricating SBS-nanoclay solid composite first and then mixing the composite with asphalt binder (composite mixing or CM). The rheological properties and storage stability of the SBS-nanoclay modified binders prepared under different conditions were tested and compared. It was found that all nanoclays increased the viscosity of SBS modified asphalt, but had insignificant effects on its rutting and fatigue properties, regardless of the mixing method. Among the three types of nanoclay investigated in this study, the one with the lowest hydrophilic property and largest layer gap performed the best, which significantly improved the storage stability of SBS modified asphalt. Between the two mixing methods, the CM method was more effective than the conventional DM method in terms of storage stability enhancement.

Keywords: Storage stability, SBS modified asphalt, Nanoclay, Mixing method

1. Introduction

Styrene-butadiene-styrene (SBS) is the most commonly used asphalt modifier, which can significantly improve the rheological and mechanical properties of asphalt binder (2011; Khodaii, 2010) However, SBS modified asphalt faces the concern of poor storage stability at high temperature due to the density difference between base asphalt binder (approximately 1.06g/m3) and SBS (approximately 0.94g/m3). According to Stoke's law (Zapién-Castillo, Rivera-Armenta, Chávez-Cinco, Salazar-Cruz, & Mendoza-Martínez, 2016), SBS has a tendency to rise in liquid bitumen, which may eventually lead to a thick congealed layer of SBS-rich phase at the surface of SBS-asphalt blends(Golestani, Nam, Nejad, & Fallah, 2015). The methods that have been applied to enhance the storage stability of SBS modified asphalt include applying sulphur additive, copolymers, functional groups and nanoclay modifiers (Fu et al., 2007). Among them, applying nanoclay is a relatively new but very attractive method, as the nano modifier can potentially improve not only the storage stability, but also various other properties of SBS modified asphalt, such as stiffness and tensile strength, thermal stability, and aging resistance.

The chemical structure of montmorillonite (MT) nanoclay is illustrated in Figure 1. It is composed of tetrahedral silicate layers and octahedral alumina layers. The tetrahedral silicate layer consists of SiO_4 groups which are linked together to form a hexagonal network of repeating units of Si_4O_{10}. The alumina layer consists of two sheets of closely packed oxygens or hydroxyls, between which octahedrally coordinated aluminium atoms are imbedded in such a position that they are equidistant from six oxygens or hydroxyls. The two tetrahedral layers sandwich the octahedral layer, sharing their apex oxygens with the latter (Liu, 2011). A single silicate layer with a sandwiched structure has a thickness of around 1 nm and a cross-sectional area of approximately100 nm^2.

In most previous studies, SBS-nanoclay modified asphalt has been prepared by directly mixing all components together, and few of these studies have focused on the storage stability of the modified asphalt (Golestani et al., 2015; Jasso, Bakos, MacLeod, & Zanzotto, 2013; Pamplona et al., 2012; Yu, Wang, Zeng, Wu, & Li, 2007). As the combination of SBS and nanoclay may be effective in reducing the density difference between SBS and base asphalt binder, one potential approach to enhance the storage stability of SBS modified asphalt is to prepare SBS-nanoclay composite first and then incorporate the composite into neat asphalt binder. The SBS-nanoclay composite can be prepared by both physical and chemical technologies, but limited application of these technologies in pavement engineering can be found in literature (Polacco, Filippi, Merusi, & Stastna, 2015). To this end, this study aims to investigate the feasibility of incorporating the SBS-nanoclay composite towards obtaining better mechanical properties as well as enhanced storage stability at high temperature. To achieve this objective, SBS-nanoclay modified asphalt samples were prepared by two different methods, i.e., the conventional direct mixing method (DM) and the novel method by preparing SBS-nanoclay composite first and then mixing the composite with neat asphalt binder (composite mixing or CM). Three types of nanoclays were selected to investigate the effects of nanoclay type. The rheological properties and storage stability of the SBS-nanoclay modified binder samples prepared under different conditions were tested and compared. In addition, X-ray diffraction (XRD) tests were conducted to observe the variation of nanoclay layer gap distance for the purpose of mechanism investigation of the interactions among SBS, nanoclay and base binder.

2. Experimental program

2.1 Materials

In this study, asphalt binder with a penetration grade of 60/70 (Pen 60/70), a common type of asphalt binder in Hong Kong, was used as the base asphalt binder to produce polymer and nanoclay modified asphalt. The dosages of SBS and nanoclay were 4% and 2% by weight of base asphalt binder, respectively, based on previous studies (Ameri, Vamegh, Imaninasab, & Rooholamini, 2016; Pamplona et al., 2012; You et al., 2011). Three different types of nanoclays (labeled as A, B, and C) supplied by Zhejiang Fenghong Clay Chemicals Co., Ltd were used, and their micro morphologies and basic properties are presented in Figure 2 and Table 1, respectively. From Figure 2, it can be observed that although the surface area of all the nanoclay was located in micrometer, the thickness of nanoclay slice was in the range of nanometre. Therefore, all of the nanoclay are nanomaterials. Among the three nanoclays, A is pure MT with Na^{+} inorganic group, while B and C are MTs having inorganic groups exchanged with different alkyl ammonium ions. The ranking of their surface hydrophilic properties from high to low is A, B, and C. SBS polymer was supplied by Kraton Performance Polymers, Inc, which is a linear block copolymer. The properties of SBS are given in Table 2.

2.2 Sample Preparation

All modified binders were prepared by a high shear mixer mixing at 180 ^{o}C with a rotation speed of 4000rpm for 2h. Three different nanoclays and two different methods were applied, resulting in in total six SBS-nanoclay modified binders. These six SBS-nanoclay modified binders were labelled as A-DM, B-DM, C-DM, A-CM, B-CM and C-CM. The first letters in these labels represent the type of nanoclay, and the last two letters represent the mixing method. Besides, the SBS modified binder without nanoclay was prepared as the control binder to investigate the effect of nanoclay; this control binder was labelled as SBSMB. When the DM method was used, nanoclay and SBS were directly mixed with hot binder by a high shear mixer. In the CM method (Figure 3), SBS and nanoclay were first dissolved and mixed in a dichloromethane solution by normal mechanical mixer at a speed of 120rpm for 20 minutes. Then, the SBS-nanoclay composite master batch was obtained by completely evaporating the dichloromethane solution. Finally, the master batch was cut into small pieces and mixed with neat asphalt binder as composite modifiers.

2.3 Testing Program

The conventional rheological tests, penetration test at 25 °C (ASTM D5) and softening point test (ASTM D36) were conducted on all modified binder samples. The rotational viscosities of the modified binders were measured at 135 °C, 150 °C and 165 °C according to AASHTO T316 using the Brookfield viscometer (model DV-II).

The mechanical performances of binders at high and intermediate temperatures were evaluated by two critical temperatures using the dynamic shear rheometer (DSR) following the performance-graded asphalt binder test according to AASHTO M320. The high and intermediate critical temperatures represent the temperature values as the rutting factor reaches 1kPa and the fatigue factor is equal to 5000kPa, respectively. Unaged samples were used for rutting resistance evaluation with a 25mm plate diameter and a 1mm gap between plates, while pressure aging vessel (PAV) aged samples were used for fatigue evaluation with a 8mm plate diameter and a 2mm gap between plates

The storage stability of each sample was characterized by four different indices, namely difference in softening point, the difference in complex modulus, the difference in fluorescence microscopic morphology, and the difference in absorbance ratio of SBS in the infrared spectrum, between the top and bottom portions of the sample after lab-simulated storage process. The ASTM D7173 procedure was followed to simulate the high temperature storage of polymer modified asphalt and to obtain the top and bottom portions of each sample. The procedure consisted of the following steps: 1) transferring the modified asphalt into an aluminium tube (with 25mm diameter and 140mm length) immediately after mixing; 2) sealing the tube and storing it vertically in an oven at 163 °C for 48 h; 3) taking the tube out of the oven and cooling it at -5 C°; and 4) cutting the tube horizontally into three equal portions and keep the top and bottom portions for storage stability testing purpose.

Figure 4 shows the flow chart for the experimental program of this study. To better understand the working mechanism of nanoclay in SBS modified asphalt, the X-ray diffraction (XRD) test was also conducted to observe the structure change of nanoclay after it was mixed with SBS and asphalt binder.

3. Results and discussion

3.1 Conventional Rheological Properties and Workability

Figure 5 and Figure 6 present the penetration, softening point and rotational viscosity test results of all binder samples. Consistent with the results of other studies (You et al., 2011), adding SBS decreases the penetration and increases the softening point of base asphalt binder. According to Figure 6, adding SBS increases the rotational viscosities at three testing temperatures, indicating reduced workability. All three nanoclays further increase the viscosity of SBS modified asphalt, but their effects on the softening point are insignificant. Different nanoclays have different effects on penetration. Only nanoclay C modified asphalt prepared by CM and DM methods increases the penetration of the SBS modified binder while others have the opposite effects. No significant difference was observed in penetration and softening point between different mixing methods.

3.2 Rutting and Fatigue Resistance

The results of two critical temperatures, indicating the rutting and fatigue performances of bitumen, respectively, are shown in Figure 7(a) and Figure 7(b) respectively.

According to Figure 7(a), the critical temperature of SBS modified asphalt is approximately 24 ^{o}C higher than that of the base binder, indicating a significant improvement of rutting resistance. However, the critical temperatures of all SBS-nanoclay modified binders are within the range of 89 ^{o}C to 95 ^{o}C, and no significant effect of nanoclay on rutting resistance can be observed. It is believed that the effect of nanoclay on rutting performance depends on both the type of nanoclay and the mixing method.

Figure 7(b) illustrates the intermediate critical temperatures of each binder. Compared with the base binder, all modified binders show a decreased fatigue resistance. The critical temperatures of all test samples are within the range of 20.5 ^{o}C to 28.5 ^{o}C, and C-DM provides the best fatigue resistance among SBS-nanoclay modified asphalt. Similar to the rutting resistance test results, it is difficult to identify the individual effect of nanoclay type and mixing method. However, generally speaking, the incorporation of nanoclay, regardless of its type or mixing method, does not significantly affect the rutting and fatigue performance of SBS modified asphalt.

3.3 Storage Stability

The main purpose of incorporating nanoclay in this study is to maintain the homogeneity of SBS modified asphalt and minimize the possibility of occurring SBS-rich phase and SBS-poor in modified binder. To investigate the storage stability of each modified asphalt, four parameters, including softening point, complex shear modulus, morphology and absorbance intensity of SBS in the infrared spectrum, were used to compare the properties of the upper and bottom portions of the modified binders after aforementioned lab-simulated high temperature storage test.

Difference in Softening Point

Among the four parameters, the softening point difference has been most commonly applied for storage stability evaluation (Fernandes, Forte, & Leite, 2008; Saeed Sadeghpour Galooyak, Dabir, Nazarbeygi, & Moeini, 2010; Polacco et al., 2015; Sun & Lu, 2003). ASTM D5892 specifies that if the difference in the softening points between the top and the bottom sections is less than 2.5 °C, the sample is considered to have good high-temperature storage stability. Figure 8 shows the testing results of softening point difference. It is clear that SBS modified binder has the worst storage performance, with a 32.4 ^{o}C softening point difference. All binders with nanoclays exhibit a better stability. The performance of A-DM and B-DM are still not satisfying since the differences are over 20 ^{o}C. In comparison, the other four SBS-nanoclay modified binders show excellent storage stability, as their softening point differences are less than 1 ^{o}C.

Difference in Complex Modulus

In addition to the traditional parameters defined in AASHTO T315, i.e., complex shear modulus (G*) and phase angle (δ), the SHRP specification defines the following separation index based on the complex shear modulus measurement:

$$I_s = \log\left(\frac{|G|^*_b}{|G|^*_t}\right) \quad (1)$$

where $|G|^*_b$ and $|G|^*_t$ are the complex shear modulus at 25 °C at a frequency of 10 rad/s of the bottom and top parts after storage, respectively.

Table 3 shows the modulus difference between the top and bottom sections and the separation indices of all test binders. A lower separation index indicates a better storage stability. According to the results, SBS has the worst storage performance, followed by A-CM, B-DM, and A-DM, while the other three binders have relatively low separation indices. Among the three types of nanoclays, nanoclay C showed the best storage stability, as the differences in both softening point and complex modulus are very small, regardless of the mixing method. Meanwhile, the modified binders prepared by the CM method generally provide a better storage performance.

Difference in Morphology

Morphology observation provides a direct impression on the SBS contents in the top and bottom sections of the modified asphalt. Fluorescence microscopy (FM) is a microscopic method, which enables the observation of polymer distribution in asphalt. The mechanism is that the aromatic phase of asphalt binder is usually the most fluorescent phase, and once the polymers absorb the aromatics, they will become bright when exposed to fluorescent light (Polacco et al., 2015). Figure 9 shows the FM images of some typical samples. The three FM images in the left column are from the samples without storage stability conditioning. For the SBS modified binder, a certain amount of SBS can be observed in the original stage. After the lab-simulated storage, much more SBS polymers show up in the top section, but very few SBS can be found in the bottom section. For nanoclay B, the top and bottom portions of B-DM after storage show similar morphologies compared with the SBS modified asphalt, while for B-CM, the observed SBS content in the top and bottom parts are relatively close to each other. The results of modified binders with nanoclay A are very similar to nanoclay B, with an obvious difference in the DM method and an insignificant difference in the CM method. For nanoclay C, samples prepared by both the DM and CM method exhibited similar SBS contents, indicating a good storage stability. The morphology test results are consistent with the softening point and complex shear modulus test results, showing that nanoclay C performs the best and the CM method is superior to the DM method. Although it only provides qualitative information, the morphology observation is still an effective method for storage performance evaluation.

Difference in Polymer Infrared Indices

According to Mouillet et al. (Masson, Pelletier, & Collins, 2001; Mouillet, Lamontagne, Durrieu, Planche, & Lapalu, 2008), Fourier transform infrared (FTIR) test results may be used to evaluate the SBS content in asphalt binder, thus evaluating the difference in SBS content between the top and bottom sections of the modified binders after storage. A typical peak of SBS is the out-of-plane bending γCH_3 vibration of trans-butadiene at 965 cm^{-1}, while one of the typical peaks of asphalt is at 1376 cm^{-1}, caused by in-plane bending vibration of δCH3. By comparing the infrared spectra of the SBS copolymers with the base bitumen, one could select their specific infrared bands not interfering with the bitumen. Then, SBS infrared indexes can be defined as the ratio of the specific copolymer absorption band to the specific asphalt absorption band. In this study, the ratio was calculated using the area under the FTIR curve. Table 4 shows the FTIR test results of each binder and their corresponding top and bottom sections after storage. The larger the absorbance ratio, the higher the SBS content of the sample. Based on the results in Table 4, in all binders except for C-CM, the top section has more SBS than the bottom section. Meanwhile, the difference in absorbance ratio between the top and bottom sections of SBS modified asphalt is the largest, followed by A-PM and B-DM. Therefore, the SBS modified binder has the worst storage stability, followed by A-DM and B-DM, while C-CM has the best storage performance. The findings of the FTIR tests are also consistent with those of the other three tests.

3.4 Mechanism Investigation

To investigate the working mechanism of each type of nanoclay when mixed with SBS and asphalt binder, XRD tests were conducted to monitor the distance between layers of nanoclays. According to Galooyak (Galooyak et al., 2010), nanoclay, after being mixed with asphalt, can act like regular particulate fillers if the distances between the clay platelets remain the same. In that case, polymer cannot enter the layer structure of nanoclays. In contrast, if the layer distances are increased, it indicates that the polymer chains have penetrated into the nanolayers, and intercalated structures are established.

The distance between the layers can be determining by the position, shape, and the intensity of the basal reflections in XRD patterns. In XRD patterns, the peak's diffraction angle corresponds to the gap distance of nanoclay, i.e., interlayer spacing of the nanoclay plates. The intensity of peak indicates the concentration of nanoclay with the corresponding gap distance. The stronger the peak's intensity is, the more nanoclay with this gap distance is located in this layer distance. In this study, the differences in nanoclays and mixing methods of SBS-nanoclay will lead to the variation of layer distance of nanoclay. Consequently, by characterizing the diffraction angle and the diffraction intensity of the nanoclays and nanoclay composites, the gap distance variation and concentration of nanoclay in the corresponding gap distance can be obtained. The basal interlayer spacing (d) can be calculated from the first strong peak in the XRD spectra by means of the following equation:

$$2 d \sin \theta = \lambda \tag{2}$$

where d is the interlayer spacing of the nanoclay platelets, θ is the diffraction angle and λ is the wavelength of the diffractometer (0.154 nm).

As shown in Figure 10(a), nanoclays A and B have only one peak while nanoclay C has two peaks at different positions. By calculation, it was found that nanoclay C has the largest gap distance between the platelets while A has the smallest, which is consistent with the information provided by the nanoclay supplier. In other words, the penetration of asphalt molecules and/or polymer into nanoclay C layers will be easier, leading to better modification performance.

Figure 10(b) shows the XRD spectra of SBS-nanoclay composites. It can be seen that all composites have larger gap distances than their corresponding original nanoclays, indicating SBS and nanoclay have formed intercalated structures. In other words, the penetration of SBS polymers enlarges the gap between the nanoclay platelets. Since SBS has lower density while nanoclay has higher density compared to bitumen, the SBS-nanoclay composite may have a density closer to asphalt binder, which contributes to the storage stability of the modified asphalt.

Figure 10(c) shows the XRD spectra of the modified binders. Peaks can be noticed in the curves of the binders prepared with nanoclay B and C while no peak was noticed for binders with nanoclay A. Based on the XRD results of the SBS modified binder and nanoclay A from Figure 10(c) and Figure 10(a) respectively, one possible explanation is that the signal of nanoclay A is hindered by the diffraction caused by the SBS in the SBS modified binder, as the peak intensity of nanolcay A is relatively low. Therefore, the nanoclay structure in the modified asphalt after interaction with the polymer is an intercalated rather than an exfoliated structure (see Figure 11). After mixing with asphalt binder, the first diffraction peaks for both nanoclays B and C were shifted towards a lower angle, which corresponds to an increase in d. Besides, the gap distances of the modified binders prepared by the CM method are larger than those in the corresponding SBS-nanoclay composites. It can also be noticed that the layer distance of the modified binders with the same nanoclay does not change when a different mixing method is used. The increase of the layer distance may be attributed to either the penetration of the SBS or asphalt component chains. It is believed that the CM method allows more interaction between SBS and nanoclay than the DM method, resulting in a better effect of the storage stability enhancement.

4. Findings and recommendations

Storage stability at high temperature is one of the major concerns of SBS modified asphalt. To address this concern, this study incorporated three types of nanoclays into SBS modified asphalt using two mixing methods (CM and DM). The rheological properties and storage stability of SBS- nanoclay modified binders prepared were tested and compared. Based on the laboratory testing results, the following findings have been obtained:

- Adding nanoclay slightly increased the viscosity of SBS modified binder, and had insignificant effects on its rutting and fatigue properties.
- Adding nanoclay to SBS modified binder leads to enhanced storage stability. Among three types of nanoclay investigated in this study, Nanoclay C with the lowest hydrophilic property and largest layer gap performed the best in terms of storage stability enhancement.
- Mixing method affects the storage stability enhancing the effect of nanoclay. The composite mixing method provided better performance than the conventional direct mixing method.

In summary, this study has shown the great potential of using the composite mixing method to prepare SBS- nanoclay modified binder with enhanced storage stability. Further studies are recommended on investigating the interaction mechanism among SBS, nanoclay and base asphalt binder when different mixing methods are used, as well as the effects of different types of nanoclay and mixing methods on the aging resistance of SBS modified asphalt.

Table 1. Physical and chemical properties of nanoclay additives

ID	Preparation process	Specific gravity	Bulk gravity	XRD d_{001}
A	Pure Na+ MMT	1.8	≤0.3	1.3nm
B	MMT modified with hydroxyl organic ammonium	1.8	≤0.3	3.0nm
C	MMT modified with double alkyl ammonium	1.7	≤0.3	3.7nm

Table 2. Characteristics of SBS

Type	Styrene-butadiene ratio	Bulk density (Kg/dm3)	Tensile strength (Mpa)	Melt flow rate (g/10min)
Linear block copolymer	30/70	0.4	33	<1

Table 3. Difference in complex shear modulus*

Binder type	Top (Pa)	Bottom (Pa)	Separation index
A-DM	1476.899	2869.927	0.289
A-CM	2134.985	2620.193	0.089
B-DM	1401.221	2502.094	0.252
B-CM	2047.217	2362.013	0.062
C-DM	1838.472	1731.798	0.026
C-CM	1562.936	1699.905	0.036
SBSMB	1265.150	2582.264	0.310

*At 25 °C and 10 rad/s

Table 4. FTIR results for storage stability evaluation

ID	Abs. 965 cm^{-1}	Abs. 1376 cm^{-1}	Absorbance Ratio

	Original binder	Top	Bottom	Original binder	Top	Bottom	Original binder	Top	Bottom
A-DM	0.076	0.083	0.077	0.123	0.118	0.127	0.616	0.709	0.603
A-CM	0.089	0.088	0.081	0.125	0.124	0.126	0.714	0.707	0.647
B-DM	0.087	0.090	0.088	0.121	0.115	0.126	0.717	0.781	0.698
B-CM	0.085	0.090	0.086	0.122	0.120	0.122	0.699	0.754	0.704
C-DM	0.085	0.083	0.075	0.120	0.119	0.107	0.710	0.700	0.699
C-CM	0.080	0.082	0.087	0.121	0.118	0.123	0.658	0.694	0.706
SBSMB	0.079	0.086	0.077	0.120	0.117	0.123	0.654	0.738	0.625

Figure 1. Structure of montmorillonite nanoclay

Figure 2. The SEM image of MT

Figure 3. SBS-nanoclay composite preparation

Figure 4. Experimental program flow chart

Figure 5. Penetration and softening point test results

Figure 6. Rotational viscosity test results

Figure 7. Critical temperatures of the modified asphalt: (a) High critical temperature; (b) Intermediate critical temperature

Figure 8. Softening point differences of top and bottom sections

Figure 9. FM images of modified asphalt before and after storage

Figure 10. XRD patterns: (a) nanoclay A, B and C; (b) Nanoclay/SBS composites; (c)SBS/nanoclay modified binder, SBSMB and base binder

Figure 11. Schematic illustration nanoclay/SBS modified binder

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