Effects of microfiller on the rheological behavior and structure of SBS modified bitumen

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Abstract. Rheological behavior of styrene-butadiene-styrene (SBS) modified bitumen with the presence of micro glass bead (GB) is investigated. It is found that either the GB fraction or size can influence the rheological property of bitumen/SBS/GB blends. Phase separation structures in all the modified bitumen systems keep a droplet-matrix type due to the sizeable compositional asymmetry between SBS-rich phase and bitumen-rich phase. The difference in the interfacial area fraction, obtained by Image J analysis reflects the effect of GB size on the rheological property. Further study on the rheology-structure correlation is put special attention on bee structure (catana phase) measured by AFM. It is found that the ratio of specific amplitude to the wavelength ($A_0/\lambda_0$) of a bee-like structure may be a valid indicator of stiffness for the modified bitumen concerning the effect of GB size difference on the rheological property. When the chemical composition is the same, the lower value of $A_0/\lambda_0$ indicates the modified bitumen with higher stiffness.

1. Introduction

Styrene-butadiene-styrene (SBS) modified bitumen has been widely investigated regarding their compatibility, microstructure, rheological property induced by phase separation [1-4]. Our previous work [5] found that with an increase of SBS addition, the phase separation mechanism would shift from nucleation-and-growth to viscoelastic phase separation, leading to a transition of phase structure from droplet-matrix structure to a viscoelastic network of SBS-rich phase. This change was determined by both compositional asymmetry and dynamic asymmetry between SBS and bitumen, which originated from the competition between SBS and asphaltenes to absorb light components [6].

Recently, the effect of silica nanoparticles, with different surface nature on the rheology and structure of bitumen/SBS blends has also been investigated [7]. It was found that the addition of SiO$_2$ nanoparticles improved the rutting resistance of bitumen/SBS blends, which was revealed by complex modulus enhancement and phase angle reduction. This improvement, in agreement with literature reports [8, 9], was strictly related to the distribution of nanoparticles and their surface nature. The blends modified by hydrophobic SiO$_2$ exhibit the better rheological property due to their more preferential attraction with bitumen, which was revealed by the apparent decrease in bee-like structure size formed.
in asphaltenes. Bee-like structures are characterized by elongated regions with alternating higher and lower bands in the surface topography of bitumen, which are surrounded by a flat area [10, 11]. The structure is also referred to a catana phase, which is immediately surrounded by a peri phase and is isolated from the para phase by the peri phase [12, 13]. The cause for the bee-like structure formation has been attracted much attention, and various possible mechanisms were proposed. For example, the bee structure was taken as a surface wrinkling, which was the result of phase separation and differential contraction due to differences in the elastic modulus of the material phases [11], or a chemically and mechanically distinct surface film that separated from the bulk bitumen [14]. In other reports, the formation of bee structure is due to the crystallization of wax or waxy molecules in asphaltenes [15, 16].

Compared with nanoparticles, the particles with microscale have lower surface free energy whose aggregation, mobility and affinity to other molecular chains will be relatively weaker. This difference would influence the rheology and structure of bitumen/SBS blends, accordingly. Besides, the effect of microparticles with a different size on the rheology and microstructure of bitumen/SBS blends is also worthy of study, which is the primary purpose of this work.

2. Materials and experiments

2.1 Materials and sample preparation

Bitumen (AH-70#) used in this paper was provided by the SK company (Korea). The fraction of saturates, aromatics, resins and asphaltenes in this bitumen were 5.9, 59.8, 19.1 and 15.2% respectively, measured by thin-layer chromatography with flame ionization detection (TLC-FID) [5, 17]. SBS (1401) was supplied by Yueyang Baling Company, Sinopec, which was a linear structure polymer containing 40% styrene by weight with $M_w$ of $10^5$ g/mol. The SBS/bitumen blends were prepared by continuous mixing of the components in toluene. The neat blend in this study is bitumen/SBS (100/4). The fraction of glass beads is 1 or 4 wt.% of bitumen. Three kinds of glass beads with a size of 2.5, 10 and 15 μm were used as microfillers without any surface modification. The samples of bitumen modified by SBS and glass beads are abbreviated as B-X%-Yμm, where X denotes the loading fraction of glass beads into bitumen/SBS blend, and Y indicates the size of the glass bead. Samples for morphological observation and rheological measurements were prepared by casting the solution on a glass slide and PTFE plate, respectively. After the removal of solvent in a desiccator and vacuum oven alternatively, these samples can be tested.

2.2 Experiments

The rheological test was performed on a rheometer (AR 1500ex, TA Instruments, USA) with 25 mm parallel plate with the fixed gap of 1 mm. A dynamic frequency sweep was carried out at 60 °C with a sweep frequency range of 0.01~100 rad/s. The strain in both kinds of experiments was kept as 1 % which is low enough to ensure the location of the linear viscoelastic region. It was necessary to note that all the rheological samples were annealed at 160 °C for 3 h, whose temperature and time was close to the usual mixing process for polymer modified bitumen in practical production [2,18].

The sample on a glass slide was annealed for 60 min under 160 °C before structure observation. The optical microscope (BK-POL-TR) was supplied by Optec Company in China. Atomic force microscopy (NX10, Park) was applied for the nano- and micro-structures observation. Height and Z-images were scanned using an etched silicon probe with a non-contact scanning mode. The resonance frequency of cantilever was 286 kHz. The sample was oscillated in the z-direction as the sample was scanned line by line at a rate of 0.5 Hz perpendicular to the cantilever. Every image was built up by 256*256 pixels each originating from the force curve evaluation.

3. Results and discussion

As shown in figure 1 (a), once the addition of glass beads into bitumen/SBS (100/4) blend, the complex modulus ($G'$) is improved in the entire frequency sweep region, no matter how large the particle size is. The $G'$ of B-1%-15μm almost overlaps with that of B-1%-2.5μm, revealing their similar rutting
resistance ability. The $G'$ at 10 rad/s of the neat blend, B-1%-2.5μm, B-1%-10μm, and B-1%-15μm systems are 29300 Pa, 46250 Pa, 52110 Pa, 44040 Pa, respectively. As a whole, the $G'$ of B-1%-10μm sample shifts slightly upward, as compared to B-1%-15μm, indicating the best rutting resistance brought by 10μm glass bead.

Figure 1. Variation of (a) complex modulus $G'$ and (b) phase angle with the frequency of bitumen/SBS/GB (100/4/1) with different GB sizes under 60 °C. The strain is kept at 1%.

The phase angle $\delta$ comparison in figure 1(b) reflects the ability of resistance to permanent deformation of materials. The $\delta$ value displays a contrary order to $G'$ that $\delta$ (B-1%-10μm) < $\delta$ (B-1%-15μm) < $\delta$ (B-1%-2.5μm) < $\delta$ (Neat). As we know, the phase angle reveals the viscoelastic balance of the material behavior, which is defined as the phase difference between stress and strain in an oscillatory test. It is noticed that the $\delta$ of all the samples are located in the region of $\delta > 45^\circ$ within the whole frequency range. This result suggests the dominant viscous response of all the SBS modified bitumen systems since the predominant viscous bitumen matrix and only 4wt.% SBS elastomer addition. The relatively lowest $\delta$ value of B-1%-10μm reflects the best resistance to rutting or deformation, consistent with complex modulus data reveals.

Based on figure 1, the addition of only 1wt.% GB into SBS modified bitumen blends can enhance their rheological property slightly, in spite of the particle size of GB. To further improve this property, the amount of GB addition is increased to 4 wt.%.

Figure 2. Variation of (a) complex modulus $G'$ and (b) phase angle with a frequency of bitumen/SBS/GB (100/4/4) with different GB size under 60 °C. The strain is kept as 1%.

As can be seen in figure 2 (a), the $G'$ of B-4%-10μm has almost improved one magnitude compared with a neat blend. All the $G'$ curves of bitumen/SBS/GB (100/4/4) blends locate above the B-1%-10μm
(solid line), whose $G^*$ value is the highest among the bitumen/SBS/GB (100/4/1) blends, according to figure 1(a). This comparison implies that the GB fraction rather than GB size plays a dominant role in complex modulus, which reflects the strength of materials. The $\delta$ variation has a contrary tendency to $G^*$. Combined with figure 2 (a) and (b), the highest $G^*$ and lowest $\delta$ of B-4%-10μm blend suggest that 10 μm has the best modification effect regarding resistance to rutting and permanent deformation.

It is known that rheological behavior depends on the structure of materials. Morphology evolution of bitumen/SBS/GB blends observed by optical microscopy after annealing under 160 °C for 60 min is shown in figure 3.

![Figure 3](image)

*Figure 3.* Morphologies of (a-a1) bitumen/SBS (100/4) blend, (b-d) bitumen/SBS/GB(100/4/1) blends, (b1-d1) bitumen/SBS/GB(100/4/4) blends. The GB size in (b-d) or (b1-d1) are 2.5μm, 10μm and 15μm respectively. The scale bar denotes 50 μm.

All the blends form a typical droplet-matrix structure in which the white and dark regions represent SBS-rich dispersed phase and bitumen-rich matrix, respectively. Upon the addition of 1% GB into the neat blend, the droplet size increased but the number of droplets reduced. According to figure 3, the area fractions of SBS-rich phase for (a-d) analyzed by Image J via using the “Make Binary” option are 46%, 15%, 12%, and 16%, respectively. Thus, although the average size of droplets in bitumen/SBS/GB is larger than that of the neat blend, the total interfacial area of droplets after phase separation is reduced after the addition of GB with different particle size, especially for B-1%-10μm. From this point of view, the compatibility between bitumen and SBS gets better after the incorporation of 1% GB particles. Besides, the excellent distribution of GB fillers in bitumen can also make a remarkable contribution to the rheological behavior. Consequently, these synergistic effects lead to a gradual improvement on rutting resistance of bitumen/SBS blends by the addition of GB, which is embodied by $G^*$ increase and $\delta$ decrease in figure 1.

The area fraction of SBS-rich phase for figure 3 (a1-d1) analyzed by Image J via the “Make Binary” option are 46, 12, 8, and 12%, respectively. This contrasting result is consistent with 1 wt.% GB filled bitumen/SBS (100/4) blends. That means the similar effect of GB particle size on the microstructure, and rheological behavior revealed by figure 1 and figure 2 either the fraction of GB is 1 wt.% or 4 wt.. It should be noted that no visible GB particles are observed on the surface of the blends either in figure 3. This may be attributed to the relatively higher density of GB particle due to their microscale size, which leads them to sink to the bottom which is covered by the bitumen-rich and SBS-rich phases.

Besides the microstructure observed by optical microscopy, the smaller structures of bitumen/SBS/GB were also investigated by AFM. Regarding the same effect of GB size on rheological properties and microstructure, only bitumen/SBS/GB (100/4/1) systems are studied by AFM. As shown in figure 4 (a-d), lots of bee-like structures (catana phase) are observed. The bee structures in each sample are not completely symmetric. Some of the bees are relatively longer and bent, as denoted by the red circle. These bent bees look like composed of two neighbor bees whose arrangement directions
has a minor angle. This appearance of bent bees is probably caused by the existence of droplet phase structure induced by phase separation between bitumen and SBS, which results in a large amplitude of surface at some region and accordingly influence the bee structure growth.

![Image](image_url)

**Figure 4.** AFM topographic (10µm*10 µm) images of (a) bitumen/SBS (100/4) blend, (b) B-1%-2.5µm, (c) B-1%-10µm and (d) B-1%-15µm blends. The bottom images are the corresponding 3D AFM results.

The 3D structure in figure 4 (a’-d’) implies that the bee structure consists of tubers [19] and chases, alternatively. It was reported that [20] the bees are caused by the surface wrinkling due to buckling of the bee laminate since this phase is stiffer and does not contract as much as the continuous matrix phase during cooling from melt temperatures. The bee laminate phase is phase separated from the bulk of the bitumen and blooms to the surface of the bitumen since the wax has a lower surface free energy.

Due to the size heterogeneity, it is difficult to compare the average size of the bee structure of bitumen/SBS blends before and after the addition of GB particles only based on figure 4. However, the number of bees for GB modified bitumen/SBS blends in figure 4(b)-(d) is more than that of the neat blend in figure 4 (a). This may be the reason for the higher complex modulus of bitumen/SBS/GB blends compared with the neat blend.

The bee structure shown in figure 4 accords with the hypothesis that bee structure is wrinkled, a stiff thin film of crystallized paraffin wax supported by a compliant substrate [11, 21]. Based on the relevant models proposed by Huang et al. [22-25], if a thin stiff film is subjected to a lateral compression strain beyond a critical compressive strain ε_c on a soft substrate, it tends to buckle into sinusoidal wrinkles with specific wavelength λ_0 and amplitude A_0 to reduce the total elastic strain energy. The characteristic factors satisfy the following equations:

\[
\lambda_0 = \frac{\pi h}{\sqrt{E_c}}
\]

\[
A_0 = h \left( \frac{\varepsilon_{\text{bee}}}{\varepsilon_c} - 1 \right)
\]

\[
\varepsilon_c = \frac{1}{4} \left( \frac{3E_s}{E_f} \right)^{2/3}
\]

where \( h \) represents the thickness of bee structure rather the whole thickness of blend film, \( \varepsilon_{\text{bee}} \) denotes the native compressive strain which could cause the wax thin film to wrinkle into bee structure, \( \overline{E_f} \) and \( \overline{E_s} \) are the plane-strain modulus of the top thin film with the existence of bee structure and that of
the substrate, respectively. The substrate material is thought to be a para phase and probably is the major material component of bitumen, which controls its bulk properties.

Further quantitative analysis of the bee structure presented in figure 4 (a-d) is given in figure 5. Taking curve 1 in figure 5 (a) as an example, the specific amplitude $A_0$, wavelength $\lambda_0$ of sinusoidal wrinkles can be derived, and the values are listed in table 1.

![Figure 5](image)

**Table 1.** Characteristic values of bee structure obtained from figure 5.

| Samples          | Lines | $\lambda_0$ (nm) | $A_0$ (nm) | $A_0/\lambda_0$ |
|------------------|-------|------------------|------------|-----------------|
| Neat No.1        | 320   | 20               | 0.063      |
| Neat No.2        | 420   | 27               | 0.064      |
| B-1%-2.5μm No.1  | 378   | 33               | 0.087      |
| B-1%-2.5μm No.2  | 444   | 35               | 0.078      |
| B-1%-10μm No.1   | 826   | 50               | 0.060      |
| B-1%-10μm No.2   | 394   | 24               | 0.060      |
| B-1%-15μm No.1   | 518   | 28               | 0.054      |
| B-1%-15μm No.2   | 482   | 45               | 0.092      |

Table 1 reveals that the height of selected bees ($2A_0$) is in the range of 40~100 nm. The previous study reported that the average height of bee structure in base bitumen is 22 ~ 85 nm [26]. This increased height of bees reveals the SBS/GB modification effect on bitumen. The characteristic size comparison has a strong dependence on the bee selection due to its size heterogeneity. To avoid this effect, it is better to compare the ratio of $A_0/\lambda_0$ instead of their value. According to table 1, the G-1%-10 μm blend has the minimum average value of $A_0/\lambda_0$. By combining equations (1) and (2), one can obtain the following equation:
Based on equation (4), smaller $A_0/\lambda_0$ values correspond to a smaller difference between $\varepsilon_{\text{bee}}$ and $\varepsilon_c$. The following discussion only emphasizes the comparison of B-1%-Yμm blend systems, to avoid the chemical component difference between the binary and ternary modified bitumen brought by GB. The $\varepsilon_{\text{bee}}$ is thought to arise naturally from the curvature elastic strain of a paraffin single crystal [21,27]. Given that $\varepsilon_{\text{bee}}$ for B-1%-Yμm systems have approximate value due to their same chemical components, there would be a positive correlation between $\varepsilon_c$ and $\frac{E_i}{E_f}$ based on equation (3). Then it can be deduced that the $A_0/\lambda_0$ would decrease as $\frac{E_i}{E_f}$ increases. The substrate is assumed to be a para phase and probably is the major material component of bitumen, which controls its bulk properties [24]. Thus, it can be deduced that smaller $A_0/\lambda_0$ values correspond to the SBS/GB modified bitumen with higher stiffness.

According to table 1, the average values of $A_0/\lambda_0$ are 0.060, 0.073, and 0.083 for B1%-10μm, B-1%-15μm, and B-1%-2.5μm, respectively. Accordingly, the stiffness values of modified bitumen $\frac{E_i}{E_f}$ can be ranged in the decreasing order as follows: B-1%-10μm > B-1%-15μm > B-1%-2.5μm. This conclusion is consistent with the resistance to deformation of B-1%-Yμm materials revealed by phase angle $\delta$ as shown in figure 1(b). To exclude the randomness of this result, we also change the scanning region for each sample and measure the other bee structures. The measurements still reveal the same trend of $A_0/\lambda_0$ comparison for the three kinds of bitumen/SBS/GB blends. This comparison suggests that the GB size can influence the characteristic size of bee structures, which reflects a difference in stiffness of B-1%-Yμm systems. The origin of structure difference in SBS modified bitumen induced by GB particles with different size is still under study. This may be associated with components interaction, phase separation behavior, and distribution or aggregation of microfillers.

4. Conclusions

In this study, both effects of GB fraction and particle size on the rheological behavior of bitumen/SBS (100/4) blends were studied. It is found that either GB fraction or GB size can influence the rutting resistance reflected by $G^*$ and $\delta$. As for the GB with a particles size of 10 μm is the best candidate modifier for the bitumen/SBS blends regarding rheological property, the phase separation structure and bee-like structure observed by optical microscopy and AFM respectively are investigated. Further qualitative and quantitative investigations on the bee structure elucidate the correlation between the ratio of specific amplitude to the wavelength of $(A_0/\lambda_0)$ the bee structure and the stiffness of bitumen materials $(\frac{E_i}{E_f})$. Roughly speaking, a lower value of $A_0/\lambda_0$ indicates the modified bitumen with higher stiffness. This conclusion is limited in the modified bitumen with the same chemical component just only difference on the GB particle size. This stiffness reflected by bee structure information is consistent with the resistance to deformation revealed by the phase angle. Thus, the $A_0/\lambda_0$ may be an effective indicator of stiffness instead of individual $A_0$ or $\lambda_0$, especially for the modified bitumen with multicomponent, in which the bee structure is liable to be influenced by many factors, such as phase separation, modifier distribution and so on.

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