Technical Paper

ISSN 1997-1400 Int. J. Pavement Res. Technol. 2(3):91-97

Study on the Relationship between Rheological Properties and Microstructure of Polymer-modified Asphalt

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Abstract: The microstructures of polymer phase in polymer modified asphalt (PMA) were obtained with the introduction of fluorescence optical microscopy. To make quantitative analysis on these microstructures, the microscopy was equipped with hardware and image analysis software. Softening point was chosen as the representative of rheological properties of PMA. Several key factors affecting the rheological properties of PMA were discussed. According to the Krieger-Dougherty (KD) model, zero shear viscosity of PMAs ($\eta_{0,PMA}$) is mainly influenced by zero shear viscosity of base asphalt ($\eta_{0,A}$), volume fraction of polymer phase (φ_P), and maximum liquid fraction (φ_m). Relationship between $\eta_{0,PMA}$ and microstructure was fully described in detail by the KD model. Factors affecting φ_P and φ_m were also discussed. Through analyzing the particle size, shape, and distribution of polymer phase in PMA, we can evaluate the mechanical properties of the mix effectively. At last, the relationship between rheological properties and microstructure of PMA was discussed and determined in this paper.

***Key words**: Fluorescence optical microscopy; KD model; Microstructure; Polymer-modified asphalt; Rheological property.*

Introduction

PMA (polymer-modified asphalt) is a heterogeneous material consisting of base asphalt, polymer modifier, and some additives. When the polymer swells completely, its mechanical properties syncretize into the asphalt. This process is called modification. In order to study the modification mechanism, many researches have been conducted. Most work focused on the rheological studies while it is difficult to reveal the molecular structure of this complicated mix.

The most valuable method for studying the morphology of this viscoelastic material is fluorescent microcopy [1]. This method can be used to determine the status of dispersion of the polymer in the base asphalt with bright yellow appeared for the polymer rich phase and dark for the asphalt rich phase.

The objectives of this paper are: 1) to observe the dispersion state of polymer in asphalt including particle diameter and area fraction of polymer; 2) to analyze the influential factors affecting the rheological properties of styrene butadiene styrene (SBS) modified asphalt; 3) to set the relationship of rheological properties and microstructure of SBS modified asphalt based on corresponding model.

Experimental and Test Method

Materials

The base asphalts are 70 penetration grade. The polymers investigated were powdered linear SBS (Kraton D1101) and powdered radial SBS (Kraton D1184). They were supplied by the Shell Chemical Company.

A container equipped with a heater, a common mixer, and a high shear mixer was used to prepare PMA samples. The base asphalt was heated in the container at 180±5℃, then SBS (5-15% weight percent) was added. The mix was continuously stirred by the high shear mixer at 1500rpm for 20minutes. Then the high shear mixer was removed and the mix was stirred by the common mixer at 200rpm for 180minutes to make polymers fully swell. The temperature of the blend was controlled at 180±5℃ during the whole procedure [2]. Though cross-linking agent is usually used to improve the properties of PMA, it was not used in this research [3] by considering that it will influence the rheological properties and microstructure of PMA. The so-formed PMAs were stored at room temperature or 163℃. Zero shear viscosity is a useful index to evaluate the performance of PMA at high temperature, but it is difficult to get large quantity of results in short period of time. Viscosity, softening point, and penetration all can provide information of stiffening effect on SBS modification [4]. Since softening point test can be performed in a simple and quick way as well as the result obtained is repetitive, softening point (Ring and Ball, R&B) is used as the index to evaluate the rheological properties instead of zero shear viscosity under the hypothesis that the higher the soften point, the larger the zero shear viscosity.

Fluorescence Optical Microscope

By far, fluorescent microscopy is the most valuable method for studying the phase morphology of PMA, as it allows the observation of structure in the raw state [1, 5]. A drop of heated PMA sample was placed between microscope slides and then observed at room temperature at a magnification level of 640×. The image was then taken by a digital camera. As shown in Fig. 1, the polymer phase is bright yellow (white in the figure) and the asphalt phase remains dark.

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Note: Submitted January 7, 2009; Revised March 3, 2009; Accepted March 9, 2009.

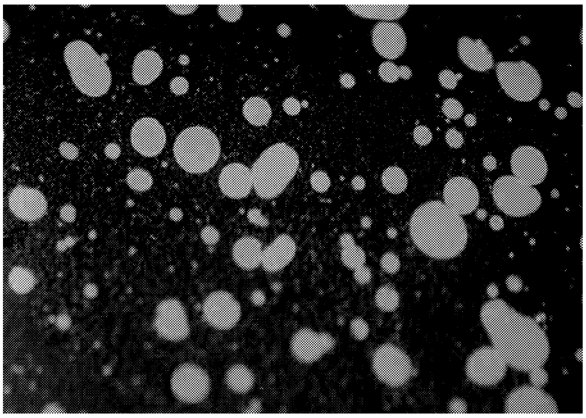


Fig. 1. Morphology of a 5% Linear SBS Modified Binder PMA Observed by Fluorescence Optical Microscopy (640×).

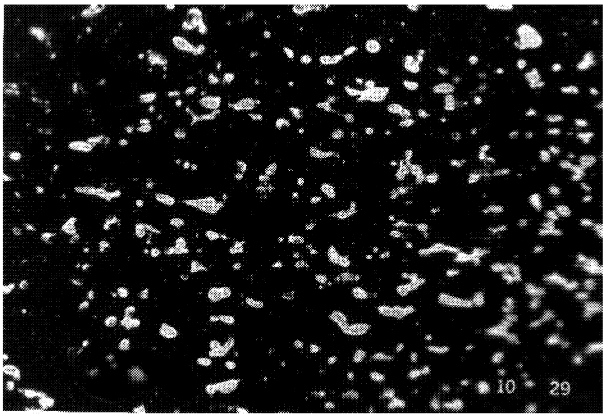


Fig. 3. Morphology of a 5% Radical SBS Polymer Modified Asphalt (640×).

Image Analysis

For microstructure obtained by Fluorescence optical microscope, image manipulation software is used to carry out quantitative analysis. A new micrograph processing system was set up by applying the integral electro-optical technology for the integration of the microscope and computer. This system consists of fluorescence optical microscopy, high-resolution camera, image acquisition, and image processing software. The whole procedure is described as follows. First the images in the fluorescence optical microscopy are transformed into video signals by camera. Then the image acquisition transforms these video signals into digital signals that can be recognized by the computer. Finally image manipulation software performs quantitative analysis on the microstructure. Professional image analysis software Image-pro Plus was used to analyze the microstructure. This software can extract important information from the captured images and has powerful analysis functions including counting and measuring. With this system, it is possible to collect large numbers of microcopies of PMAs and perform quantitative analysis rapidly and accurately.

Results including phase area, particle diameter, shape of polymer phase, percent area of polymer phase and more are generated automatically and reported in this paper. Fig. 2 is a typical interface of analysis on microcopy of PMAs. Results such as max diameter of polymer phase, 52μm; average diameter of polymer phase, 8.7μm; percent area of polymer phase, 22.0%; total amount of particles, 87 are shown in Fig. 2. The shape of polymer phase has a great impact on the rheological properties of PMA, and this can also be obtained from this software. The characteristic parameter of polymer shape is collected and then expressed in numerical value (The minim value is 1, standing for the sphere polymer phase, and the larger the value, the more irregular in the shape.). In Fig. 1 shape of polymer phase is 1.4.

Phase Characteristics of So-Formed PMA

Continuous Asphalt Phase with Dispersed Polymer Rich Phase

Fig. 3 shows a radical SBS modified asphalt. Compared with Fig. 1, it is clear that linear SBS particle presents as regular sphere and radial SBS particle presents as irregular stripe shape in asphalt matrix.

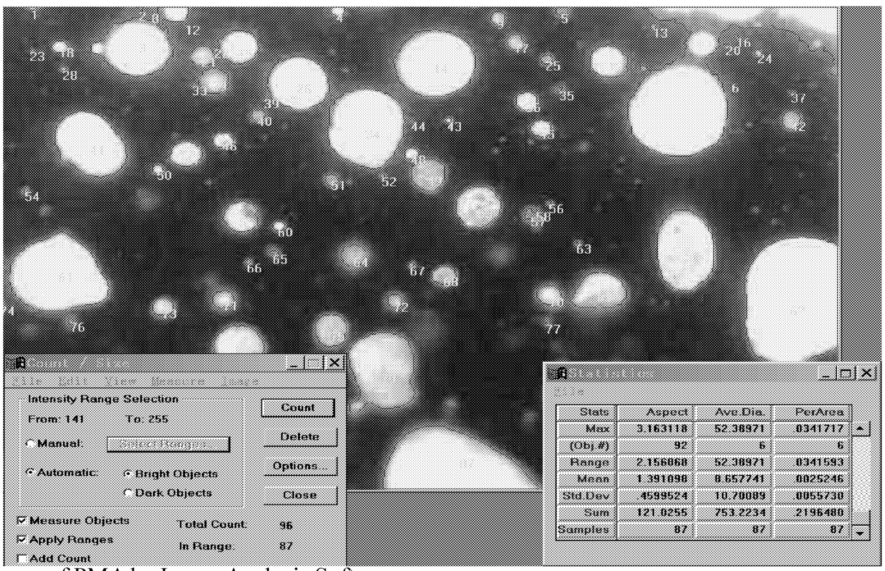


Fig. 2. Results of Microcopy of PMA by Image Analysis Software.

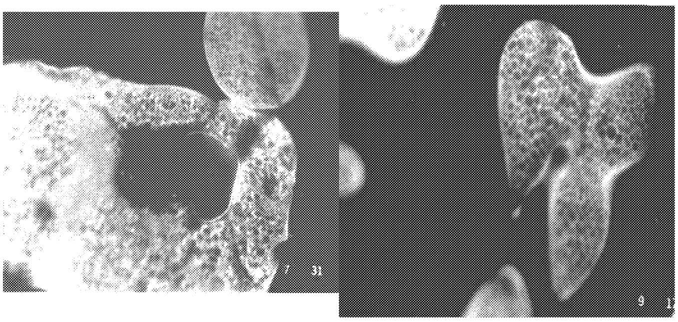
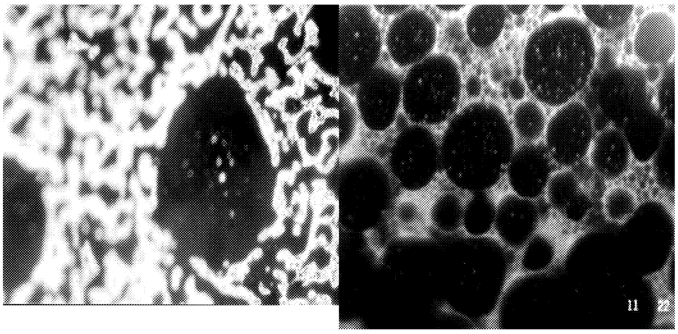


Fig. 4. Cell Structure with a High Value of Separation for 5% Linear SBS Modified Inferior Quality Base Asphalt PMA (640×).



(a) (b)

Fig. 5. Continuous SBS Rich Phase (640×) for (a) 15% and (b) 7% Radial SBS Modified Asphalt PMA.

A complicated morphology is shown in Fig. 4, and the tiny droplet of asphalt contained in the dispersed polymer particle is observed. This phenomenon is described as the cell structure. PMA with this structure usually shows bad storage stability.

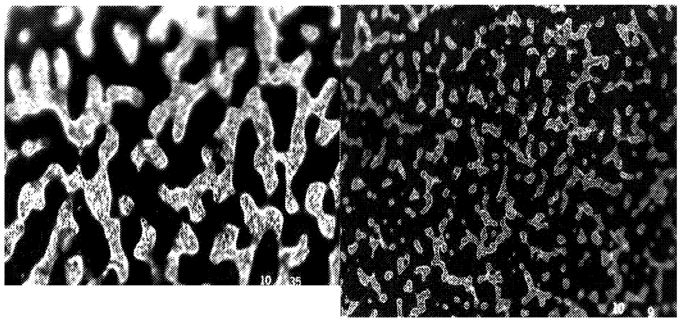
Figs, 1, 3, and 4 illustrate a similar system that has an asphalt rich phase with a homogeneous dispersion of polymer sphere. As for SBS modified asphalt, asphalt rich phase system is usually defined as the content of SBS less than 5% (in weight).

Continuous Polymer Rich Phase with Dispersion

Fig. 5 shows a typical continuous polymer rich phase structure. This structure appears when SBS content is very high (7wt% or higher). In General, when two phases are mixed together, continuous phase stands for the high content phase and low content phasepresents as dispersed phase. Theoretically, when a phase accounting for more than 74% volume percent, it is bound to be continuous phase. Namely, the other phase is defined as dispersed phase. In SBS modified asphalt, although SBS content is just 7% or more, the elastomeric phase of SBS absorbs the oil fractions from the asphalt and swells up to nine times as much as its initial volume [6]. Thus 7% content of SBS can presents as continuous phase.

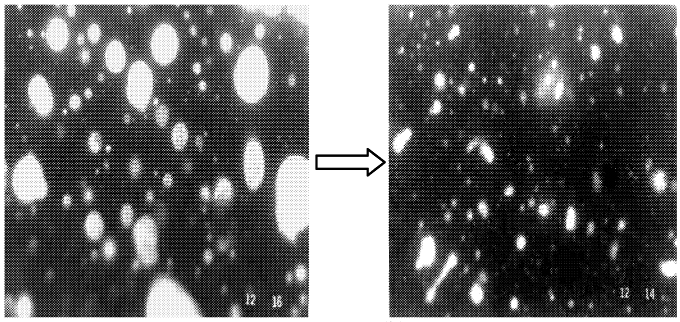
Two Interlocked Continuous Phases

When asphalt content is about 6%, two interlocked continuous phases are produced. In this situation, asphalt phase and SBS phase are interlocked and both are continuous (Fig. 6). This structure is an ideal microstructure and may change to continuous SBS rich phase



(a) (b)

Fig. 6. Two Interlocked Continuous Phases (640×) for (a) 7% and (b) 5% Radial SBS Modified Asphalt PMA.



(a) Area Percent：21.8% R&B Softening Point：70℃

(b) Area Percent：7.0% R&B Softening Point：58℃

Fig. 7. Morphology at Different Time (a) Before and (b) After Four Months for 5% Linear SBS Modified Asphalt PMA (640×) Stored at 25℃ without Stirring.

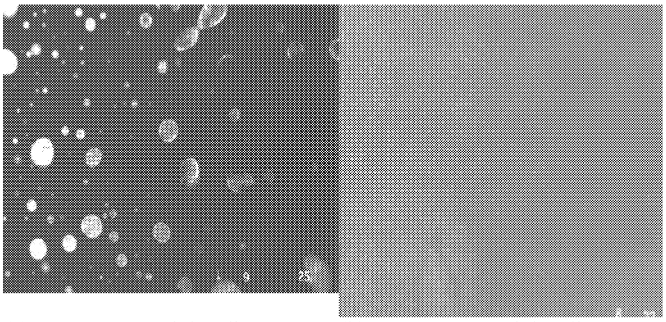
or continuous asphalt rich phase structure according to mixing temperature, SBS quality, and so on.

Major Factors Influenced on Rheological Properties of PMA

The rheological properties of PMA are different from those of original asphalt. With the rheological properties of polymer syncretizing into the asphalt, the mechanical properties of PMA are improved. However, no analogous theory and model are available to explain how the rheological properties being modified. Factors affecting the rheological properties of PMA as well as the influential degree are unknown. In theory, structure determines the mechanical properties of the material. Hereby, the structure of polymer phase in the PMA plays a key role in the rheological properties of PMA.

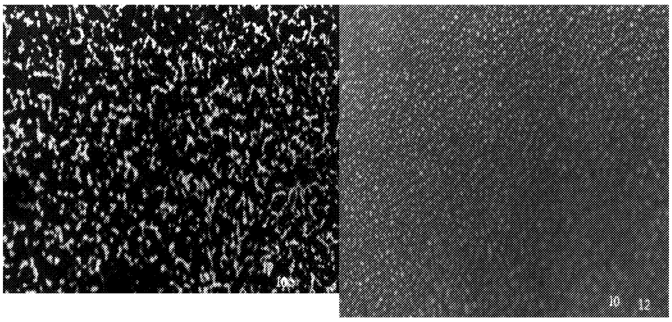
With fluorescence optical microcopy, we can obtain various microstructures of polymer phase in the PMA. Then the corresponding softening point (R&B) is tested. Some factors that greatly influencing on the rheological properties of PMA are drawn from the comparison of softening point (R&B) and microstructure of polymer phase in the PMA and are stated below:

1. The more area fraction of polymer phase the PMA has, the higher its softening point is. Moreover, the higher the SBS content in the PMA, the higher the softening point. As shown in Fig. 7, a SBS modified asphalt stored at room temperature for four months was examined. Results indicate that area fraction of polymer phase decreased from 21.8 to 7.0% and softening



(a) Average particles diameter: 8.2μm,Softening Point: 73℃ (b) Average particles diameter < 1μm, Softening Point: 58℃

Fig. 8. Microscope Images Obtained at Different Storage Time (a) 1hr and (b) 48hrs for 5% Linear SBS Modified Asphalt PMA (640×) Stored at 163℃ without Stirring.



(a) Average Particles Diameter: 19.3μm, Softening Point: 95.5℃ (160×) (b) Average Particles Diameter: < 1μm, Softening Point: 66.5℃ (640×)

Fig. 9. Microscope Images Obtained at Different Storage Time (a) 1hr and (b) 48hrs for 5% Radial SBS Modified Asphalt PMA Stored at 163℃ without Stirring.

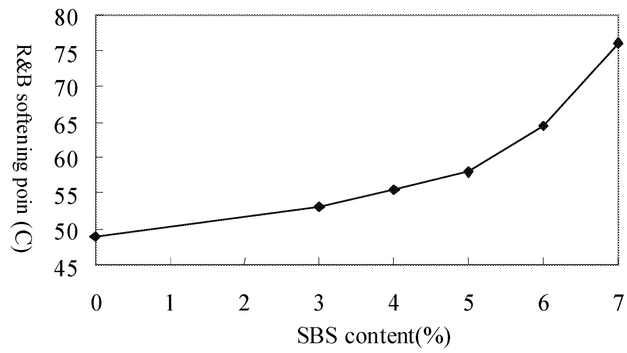


Fig. 10. Relationship between SBS Content and Softening Point for 5% Linear SBS Modified Asphalt PMA.

point (R&B) also fell from 70 to 58℃.

2. PMA with larger particle diameter has a higher softening point (R&B) when other factors are the same. Fig. 8 presents different microstructures of the same linear SBS modified asphalt at different storage time.

   The softening point (R&B) of PMA in Fig. 8(a) is higher than that in Fig. 8(b). The sharp difference in softening point (R&B) is due to the change of particle diameter of polymer phase. By comparing their microcopies, we can see that the particle diameter of polymer phase in Fig. 8(a) is bigger than that in Fig. 8(b). Fig. 9 shows the microcopies of the same radial SBS modified asphalt at different storage time. Similar results are observed. The bigger the particle diameter is, the higher the softening point is.

3. Figs. 8(a) and 9(a) show the microstructure of the polymer phase in PMA for linear SBS modified asphalt and radial SBS modified asphalt respectively. We can see that linear SBS phase is mostly in sphere shape while radial SBS phase is mostly in irregular strip shape. Consequently, the softening point(R&B) of PMA in Fig. 9(a) is nearly 20℃ higher than that in Fig. 8(a).

Relationship between Rheological Properties and Microstructure and KD Model

Essentially, PMA is a suspension where polymer phase behaves as solid phase and asphalt phase behaves as liquid phase. More than one hundred empirical models were set to explain the relationship between suspension rheological properties and structure in Rheology [7]. According to non-Newtonian fluid suspension theory, the relationship between structure and viscosity in PMA suspension can be described as follows, $\eta_{0,PMA}$ (zero viscosity of PMA) will increase with the increasing of φ_P (volume fraction occupied by polymer phase in PMA suspension). The relationship between $\eta_{0,PMA}$ and φ_P is linear when φ_P is small. As φ_P increases, $\eta_{0,PMA}$ becomes non-linear related to φ_P. Finally when $\varphi_P \rightarrow \varphi_m$ (maximum value of φ_P attainable by a given collection of particles under given conditions of flow), $\eta_{0,PMA}$ tends toward infinity.

φ_m is function of particle shape. For sphere particles the upper bound of φ_m is 0.74. When polymer phase is in irregular form such as slender body; the value of φ_m decreases rapidly. For example, φ_m can decreases to 0.081 when the ratio of length to diameter, L/D, reaches 60. According to above relationship, when φ_P is close to 0.081, the viscosity will trend to infinite.

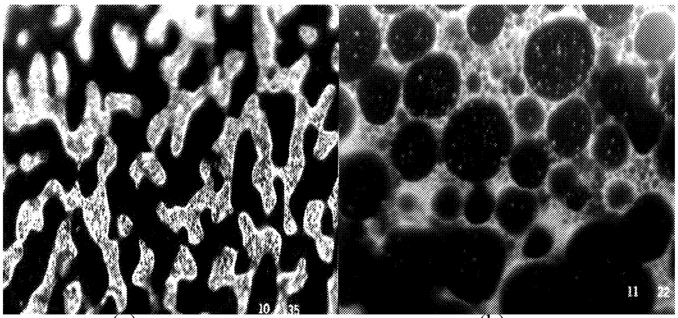
Although the content of SBS in asphalt is generally between 3 and 7%, its φ_P is very high in asphalt. That is because SBS will swell in asphalt and absorb substantial oil fraction (up to 8 times of itself volume), forming polymer phase [8]. For higher φ_P, particularly as $\varphi_P \rightarrow \varphi_m$, Kriege-Dougherty (KD) model is the most successful model to describe the relationship between rheological properties and solid phase fraction [9]. Storm and Sheu ever proposed a colloidal model according to KD model to explain the temperature dependence of asphalt zero-shear viscosity [10].

KD model is a rheological equation describing the relationship between rheological properties of PMA and microstructure of polymer phase and can be presented by Eq. (1)

$$\eta_{0,PMA} = \eta_{0,A}[(1-\varphi_p/\varphi_m)^{-2}] \quad (1)$$

where $\eta_{0,PMA}$ = zero shear viscosity of PMA; $\eta_{0,A}$ = zero shear viscosity of base asphalt; φ_p= volume fraction occupied by polymer phase in PMA suspension, called solid fraction; and φ_m = maximum value of φ_P attainable by a given collection of particles under given conditions of flow [9].

According to KD model, $\eta_{0,PMA}$ is influenced by $\eta_{0,A}$ as well as by φ_p and φ_m. Based on the analysis of KD equation, the influence ofφ_p and φ_m on $\eta_{0,PMA}$ can be concluded as follows:



(a) $\varphi_P \rightarrow \varphi_m$ (b) $\varphi_P = \varphi_m$

Fig. 11. Influence of Linear SBS Contents (a) 6% and (b) 15% on Softening Point.

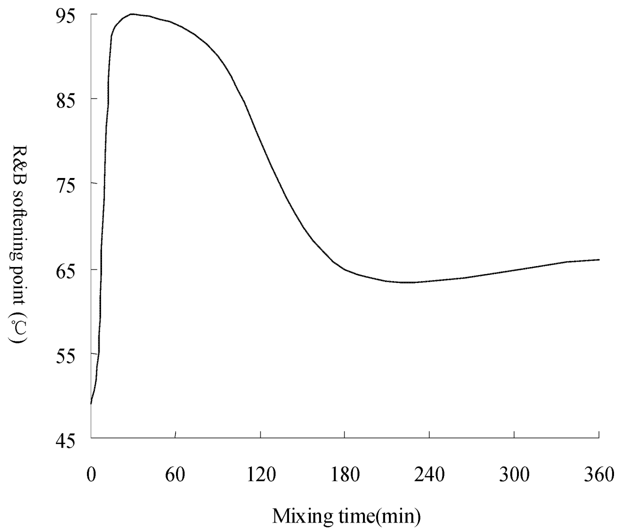


Fig. 12. Relationship between Softening Point and Mixing(Stirring) Time.

1. $\eta_{0,PMA}$ will increases with the increasing of φ_p and their relation is not linear. Especially when φ_P tends to φ_m, a small increment of φ_p may cause a sharp increase of $\eta_{0,PMA}$. The influential factors on φ_p include polymer content and polymer swelling ratio in asphalt.
2. The smaller φ_m is, the bigger $\eta_{0,PMA}$ is. Because in this situation it is easy for φ_p to get close to φ_m, resulting in the increasing of $\eta_{0,PMA}$.
   (1) The shape of polymer phase in PMA has a great influence on φ_m. When polymer phase is in tripe or other irregular shapes, φ_m shows a small value.
   (2) Compared to asphalt phase, polymer phase is solid phase, however, polymer phase varies in hardness. In general, soft polymer phase deforms easily in shear field, resulting in high φ_m and thus low $\eta_{0,PMA}$; The reduction of particle diameter reduces the difference between polymer phase and asphalt phase, and causes the polymer phase to degrade easily. As a result, polymer phase becomes much softer. Ultimately, $\eta_{0,PMA}$ decreases while φ_m increases.

With the image analysis software, polymer phase area fraction of PMA is available, whereas only volume fraction can be adopted in KD model. According to Stereology theory [11], when bidimensional image represents section rather than reflection, each area fraction is equal to volume fraction. The microcopy of polymer phase obtained by fluorescence optical microscopy is section rather than reflection, thus:

$$\Phi_{PV} = \Phi_{PA} \tag{2}$$

where Φ_{PV} = volume fraction of polymer phase in PMA; and Φ_{PA} = area fraction of polymer phase calculated by image analysis software according to microcopy obtained by fluorescence optical microscopy.

Since area fraction of polymer phase calculated by image analysis software is equal to volume fraction of polymer phase in PMA, relationship between $\eta_{0,PMA}$ and microstructure can be set by KD model.

Because $\eta_{0,PMA}$ is difficult to obtain, softening point (R&B) is used to describe the rheological properties of PMA instead of $\eta_{0,PMA}$. The higher softening point (R&B) is, the higher $\eta_{0,PMA}$ is.

Explanation and Discussion

As presented in Fig. 10, the softening point(R&B) of SBS modified asphalt changes as the SBS content increases.

The curve in Fig. 10 can be divided into two stages. First, when SBS content increased from 3 to 5%, softening point (R&B) increased steadily and the relationship was almost linear. In the second stage, SBS content increased from 5 to 7% and the softening point (R&B) increased exponentially.

With the increase of SBS content, volume fraction of polymer phase increases and sequentially softening point (R&B) increases. So a slight change in SBS content may cause great change in $\eta_{0,PMA}$. As a result when the SBS content increases from 5 to 6% and finally to 7%, the gradient of softening point (R&B) curve is always increasing. When SBS content reached 6% as is shown in Fig. 11(a), microstructure may be formed in which the two phases (polymer phase and asphalt phase) are continuous and interlocked, it means that $\varphi_P \rightarrow \varphi_m$. As SBS content ultimately reaches 7%, φ_P also reaches φ_m. As shown in Fig. 11(b), the polymer phase is a continuous phase. Meanwhile, softening point (R&B) exceeds 90℃, corresponding to $\eta_{0,PMA} \rightarrow \infty$ consequently.

The category of SBS has a great influence on the rheological properties of PMA. With the same producing process, PMA modified by linear SBS differs from that by radial SBS while both SBS content is 5%. The softening point (R&B) of the linear SBS based PMA is 73℃ (Fig. 8(a)) while that of the radial SBS based PMA reaches as high as 95.5℃ (Fig. 9(a)).

Under the same condition, softening point (R&B) of radial SBS modified asphalt is much higher than that of linear SBS modified asphalt. The difference is due to the different shapes of SBS, as shown in Figs. 8(a) and 9(a). The linear SBS phase is in regular sphere with high φ_m while radial SBS phase is in irregular strip shape with low φ_m.

The same PMA presents different rheological properties over mixing time. For example, after mixed into 5% SBS, the softening point (R&B) of asphalt over mixing time can be described in Fig. 12.

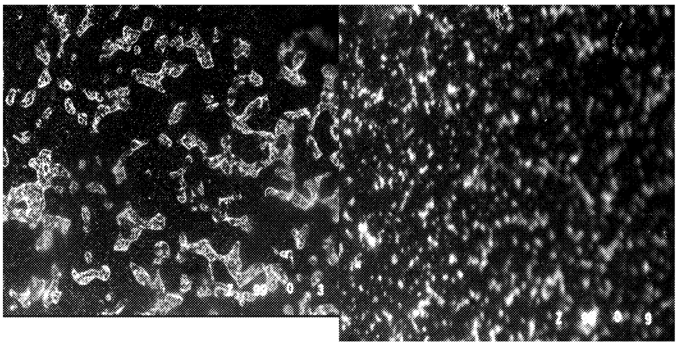

(a) (b)

Fig. 13. Influence of TFOT on 5% Radial SBS Modified Asphalt PMA (640×) (a) Original PMA, R&B Softening Point: 91℃ and (b) PMA after TFOT, R&B Softening Point: 65℃.

From Fig. 12, we can see that with the mixing time of PMA increasing, its softening point (R&B) increased from 48℃ to peak value 95℃, and then fell to 66.5℃ as the mixing continuing.

There is an increasing and falling tendency during the mixing of SBS with asphalt. This phenomenon can be explained by KD model reasonably. In the initial period while SBS has not swelled enough in asphalt, φ_P is so small that softening point (R&B) is very low. As the mixing procedure continuing, SBS swells totally and φ_P increases, resulting in the rising of softening point (R&B) (as shown in Fig. 9(a)). The particle diameter begins to decrease when further mixing continues (as shown in Fig. 9(b)), resulting in the increase of φ_m. Thus softening point (R&B) is bound to drop.

There is an abnormal phenomenon with softening point (R&B) of SBS modified asphalt after TFOT (thin film oven test). While softening point (R&B) will improve for base asphalt after TFOT, SBS modified asphalt shows an obvious decrease in its softening point (R&B), from 91 to 65℃, as shown in Fig. 13.

Two aspects are involved concerning the decreasing in softening point (R&B) of PMA after TFOT. On the one hand, the particle diameter of polymer phase decrease as shown in Fig. 13(a) (original PMA) and Fig. 13(b) (PMA after TFOT); on the other hand, polymer degrades because of TFOT. Both factors can reduce the softening point (R&B).

As stated previously, various complicated rheological properties are successfully explained by KD model. Furthermore, many other complicated rheological phenomena can also be explained by this model [12]. According to the relationship between the microstructure and the macro-performance, a simple and convenient method for the quality control of modified asphalt can be obtained [13].

Conclusions and Future Work

In terms of phase character, there are three types of structure in SBS modified asphalt, continuous asphalt phase with dispersed polymer rich phase, continuous polymer rich phase with dispersed asphalt phase, and two interlocked continuous phases. The phase morphology of SBS modified asphalt is the result of the mutual effects of SBS and base asphalt and is influenced by SBS type and its content. For the investigated PMAs, phase inversion from a continuous asphalt phase to two interlocked continuous phase occurs when SBS content is 5%, and when SBS content is more than 7% the morphology presents as continuous SBS phase. In general, SBS content and its quality determine the phase structure of PMA.

Fluorescence optical microscopy can help to obtain many microscopy images with high repeatability, combined with hardware device for digital processing and image analysis software, it is possible to make analysis on the microstructure of PMA.

The area fraction, particle diameter, and shape of polymer phase in SBS modified asphalt are three main factors that influence its rheological properties.

The KD model given as $\eta_{PMA} = \eta_A[(1-\varphi_p/\varphi_m)^{-2}]$ can explain various complicated rheological phenomena in SBS modified asphalt, and can be used to explain its rheological properties based on its microstructure.

The conclusion of this study covers the utilization of one type of penetration grade asphalt and two types of SBS. More research should be carried out by using various SBS and base asphalt. Only softening point (R&B) was used to indicate the rheological property in this study, more indexes should be introduced in further research.

Acknowledgements

The authors would like to express their sincere thanks to the National Science Foundation of China of funding this research project (Grant No.59778049).

Declaimer

The information in this paper only reflects the views of the authors. No official endorsement should be associated with the information provided.

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