

Storage stability and compatibility of asphalt binder modified by SBS graft copolymer

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Abstract

The performance of styrene–butadiene–styrene (SBS) triblock copolymer modified asphalt binder at high temperature can be improved significantly with the addition of SBS-g-M grafted with vinyl monomer under γ -rays irradiation. The dynamic mechanical properties of SBS modify asphalts binder before and after graft has been characterized by use of dynamic shear rheometer. It has been found that the added content of SBS-g-M has great effect on the rheological properties of the binder and its high temperature performance was improved while its temperature susceptibility was reduced in compare with SBS modified asphalts binder. It also has been confirmed that the morphology observed by fluorescence microscopy revealed the compatibility between SBS-g-M and asphalt and the storage stability of binder was improved significantly compared with SBS modified asphalt binder. As a consequence, the use of SBS grafted with polar monomer can be considered a suitable alternative for modification of binder in pavement.

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1. Introduction

The use of polymer modified asphalt (PMA) to achieve better asphalt pavement performance has been observed for a long time [1]. The improved functional properties reveal in following aspects such as permanent deformation [2–5], fatigue and low temperature cracking [6], stripping [7], wear resistance [8], ageing [9] and so on. The properties of PMA are largely dependent either on the polymer characteristics and content or asphalt nature, as well as the blending process [10]. Despite the large number of polymeric products used, there are relatively a few types suitable for asphalt modification. When the polymer was used as asphalt modifiers, the selected polymers should be compatible with asphalt in blended process with conventional mixing equipments and can maintain their main properties.

Two classes of polymers, elastomer and plastomer, are typically used in asphalt modification. It has been identified that styrene–butadiene–styrene triblock copolymer (SBS) can obviously improve the mechanical properties and rheological behavior of conventional asphalt compositions [11]. As it is provided with a two-phase morphology consisting of glassy polystyrene (PS) domains connected together by the rubber polybutadiene (PB) segments at the temperatures between glass transition temperatures of PB and PS, SBS shows itself crosslinked elastomer network behavior. Above the glass transition temperature of PS, the PS domains soften and SBS becomes melted to suitable for process. This property of a thermoplastic elastomer has allowed SBS to become one of the promising candidates in asphalt modification [12].

Asphalt may present either elastic or viscous behavior, or a combination of both, depending on the temperature and the time over which the asphalt is observed. An adequate viscoelastic response of the asphalt is fundamental to ensure a good performance of the road pavement. This

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aspect has been stood out by the SHRP Highway Research Program [2] which proposes a novel set of tests, many of them involving rheological methods, to replace conventional less reliable trials. The major concern of asphalt/polymer blends is their lack of stability during prolonged storage at high temperatures. The tendency to phase separation under quiescent conditions appears as an important limitation for the practical use of these blends [11,13].

As a part of our long-term interest in the studies on the performance modeling of asphalts using grafted SBS by irradiation method, we are investigating the relationship between asphalt and polymer using ageing test (RTFOT), ductility, and chemical properties. In this article the main objective is to characterize the fundamental properties (i.e. morphology, rheology and compatibility) of modified asphalt by SBS with addition of monomer M, and to study the effect of content on the rheological characteristic of the asphalts.

2. Materials and methods

2.1. Materials

SBS (Grade 791): was produced by the Yueyang Petrochemical Co., Ltd., China. It was a linear-like SBS, containing 30 wt% styrene, and the weight average molecular weight was 150,000 by GPC. SBS was modified by polar monomer, such as methacrylic acid by ^{60}Co γ -rays radiation method, and the graft degree of SBS-g-M was about 6%, the detail procedure was referred as the literature [14].

Taiwan CPCA-H-70 was obtained from Wuxi Road Department, Jiangsu, China. The physical properties of this asphalt are as follows: softening point: 45.2 °C (ASTM standard D36), penetration: 91 dmm (25 °C, ASTM standard D5); viscosity: 378 Pa s (135 °C, ASTM standard D4402), and fractional composition (6% saturates, 37% aromatics, 46% resins, 11% asphaltenes).

2.2. Preparation of sample

Asphalt was heated to 160 °C in a small container until it flowed fully. A given part of SBS or SBS-g-M (based on 100 parts asphalt) was mixed into the asphalt under high-speed stirring for 40 min and the blend became essentially homogenous. Mixing was then continued at 160 °C with low-speed stirring for 30 min.

2.3. Storage stability test

The storage stability of asphalt binder was tested as follows. The sample was poured into an aluminum foil tube, 30 mm in diameter and 15.0 cm in height. After closing the tube without air enclosure, it was stored vertically 163 °C in an oven for 48 h. Then the tube containing the modified asphalt was cooled to ambient temperature and cut horizontally into three equal sections. The difference in softening points between the top and the bottom sections

of the tube was measured. When the difference was less than 2.5 °C, the sample could be regarded as having good storage stability.

2.4. Rheological characterization

A strain-controlled rheometer (Advances Rheology Expanded System, ARES of Rheometric Scientific Co., USA) with parallel plate geometry (25 mm in diameter) was used to determine the rheological characterization of polymer modification asphalt (PMA). A temperature sweep was applied over the range 0–100 °C at a fixed frequency of 10 rad/s and variable strain. The strain amplitude for all the tests was confined within the linear viscoelastic (LVE) response of the binder. A sample of about 1.0 g was heated to flow, the upper parallel plate was lowered to contact tightly with the sample and the sample trimmed. The final gap was adjusted to 1.2 mm. All samples were held at a defined, constant temperature for 15 min and then the temperature varied in 5 °C increments. Various viscoelastic parameters, such as G^* , G' , G'' and $\tan \delta$ were collected automatically by the RSI Orchestrator software.

The principal viscoelastic parameters obtained were the complex modulus (G^*) and the phase angle (δ). G^* is defined as the ratio of maximum (shear) stress to maximum strain and provides a measure of the total resistance to deformation when the asphalt is subjected to shear loading. It contains elastic and viscous components, which are designated as the (shear) storage modulus (G') and shear loss modulus (G''); respectively, expressed as $G^* = G' + iG''$. These two components are related to the complex modulus and to each other through the phase (or loss) angle (δ) which is the phase, or time, lag between the applied shear stress and shear strain responses during a test. The phase angle, defined above as the phase difference between stress and strain in an oscillatory test, is a measure of the viscoelastic balance of the material behavior. If δ equals 90° then the bituminous material can be considered to be purely viscous in nature, whereas of 0° corresponds to purely elastic behavior. Between these two extremes the material behavior can be considered to be viscoelastic in nature with a combination of viscous and elastic responses.

2.5. Fluorescence microscopy

The sample properties were observed using a Fluorescence microscope, made by Nicro Co., Japan. The modified asphalt was illuminated using a blue light for excitation and the fluorescent yellow light re-emitted by the swollen polymer phase was observed using an optical microscope. The instrument was equipped with a Polaroid camera and a blue filter system. The wavelength of excitation is in the range 390–490 nm. Thin slide of modified asphalts were prepared using very small amounts of the heated sample and viewed under the microscope with a magnification of 100× at room temperature.

3. Results and discussion

3.1. Viscoelasticity of modified asphalts with SBS and SBS-g-M

It was considered quite interesting to compare the rheological behaviors with base asphalt, SBS-modified and SBS-g-M modified asphalts as shown in Fig. 1. The three asphalts show similar linear viscoelastic behaviors and functions at 0 and 90 °C. The G^* of the original asphalt decreased sharply with increasing temperature and is very low at high temperature, while $\tan \delta$ of the original asphalt dramatically increases at the same time. The phase angle (δ) of the original asphalt approaches 90° at temperature of 100 °C. In this case, the stored energy per cycle of deformation becomes negligible, so at this time asphalt exhibits nearly pure viscous liquid behavior without any elasticity. However, the varying trend of $\tan \delta$ and G^* was slowed down while 5% SBS mixed with the asphalt. The similar phenomenon has been reported in an early publication by Lu and Isacsson [11]. Nevertheless, the graft of monomer in SBS led to the increase in G^* more significantly at higher temperatures, and the $\tan \delta$ curve became flatter in a wide range of tested temperatures. It indicated that the elasticity of the modified binder had been improved effectively with the graft of monomer in SBS due to the formation of a crosslinked network in the modified binders.

The Strategic Highway Research Program (SHRP) tests, developed to replace old conventional tests, made efforts to take advantage of the rheological measurements to analysis the ultimate properties of bitumen binders used in road pavements, which adopted the temperature of the modified asphalts when $G^*/\sin \delta$ is equal to 1 kPa as a criterion for the asphalt binder at high temperature [2,15,16]. As shown in Table 1, when $G^*/\sin \delta$ was equal to 1000 Pa the temperature of asphalt binders was 67.5 °C for base asphalt, 78.2 °C for PMA with addition of 5.0% SBS, 82.4 °C for

PMA with addition of 5.0 % SBS-g-M, respectively. It is found that the modified asphalts binder added with grafted SBS have higher performance than that added with pure SBS and base asphalt. It is known that SBS was non-polar polymer. When modified in irradiation grafting method by vinyl monomer, such as methacrylic acid, the copolymer with some polarity made the inter-effect between it and asphalt very strong. And the storage stability of PMA can be obviously enhanced.

3.2. Effect of SBS-g-M content

The rheology of modified asphalt binder is strongly dependent on added content of polymer. As recorded in Fig. 2, at a low added content of grafted polymer (3%), the behavior of the modified binders remains close to that of the base asphalt. After modification with a sufficient content of grafted polymer ($\geq 6\%$), the binders change fundamentally in their rheological behavior by a substantial decrease in phase angle and increase in complex modulus. At higher SBS-g-M content, $\tan \delta$ of the modified asphalts is very small and changes very slightly at a given temperature Meanwhile the complex modulus (G^*) of PMA increases. In these cases, the rheological response of the modified binders could be related to the formation of network structure of polymer.

The T_{SHRP} of the modified asphalt binder can be calculated when $G^*/\sin \delta$ is equal to 1 kPa and is dependent on the SBS-g-M content as shown in Table 2. The one of

Table 1
The performance of SBS and SBS-g-M modified asphalt

Sample	$T_{SHRP}/^{\circ}\text{C}$
Base asphalt	67.5
PMA by 5% SBS	78.2
PMA by 5% SBS-g-M	82.4

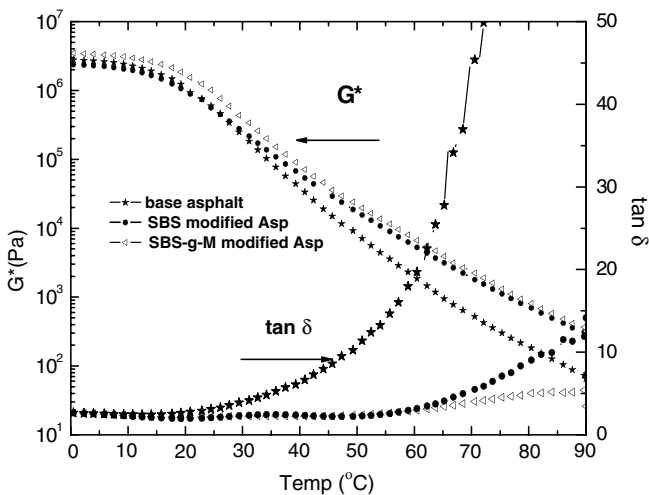


Fig. 1. Complex modulus (G^*) and $\tan \delta$ versus temperature for base and modified asphalt at 10 rad/s.

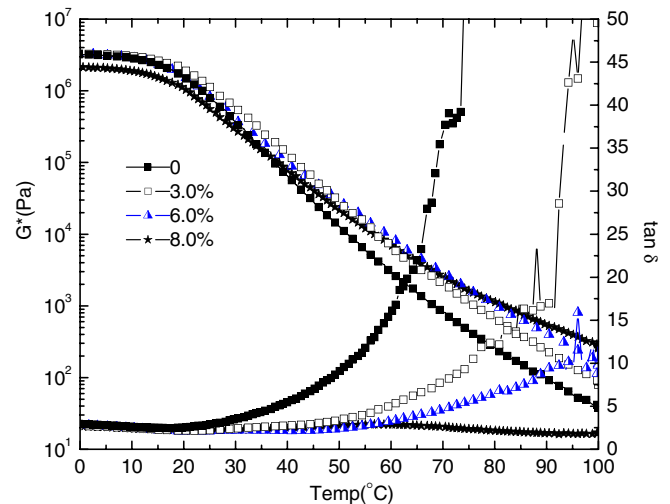


Fig. 2. Effect of SBS-g-M content on dynamic mechanical properties of PMA.

the PMA added with 8% of SBS-g-M may be best, which cannot be performed with virgin SBS at content of 8%.

3.3. Storage stability of PMA by SBS-g-M

Due to the difference in the solubility parameter and density between SBS and asphalt, phase separation would take place in general SBS modified asphalt binder during storage at higher temperatures. Droplets of the melted polymer dispersed in asphalt are usually accumulated and float on the top of the asphalt binder at a high temperature under static situation. As mentioned earlier the difference in softening points between the top and the bottom sections of the tube was measured as isolation degree of binder. The isolation degree of PMA binder added with 6% SBS-g-M changed from 1.5 °C for fresh prepared binder to 2.3 °C for binder stored for 4 month at room temperature. And with the binder added 8% of SBS-g-M the isolation degree changed from 0.2 °C for fresh prepared binder to 1.2 °C for stored 4 months at room temperature. Anyway, the differences of softening point between the top and bottom sections measured according to the rule of isolation degree measurement were not more than 2.5 °C as listed in Table 3. It can be deduced that fresh prepared asphalt binder can be used in pavement at once and can be store at room temperature for long time and then melted again for further uses, which is very convenient for user. Ordinary the measurement of isolation degree is made just after preparation of binder and there is little report about results with modified asphalt binder stored for 4 months. In fact, the softening point of modified asphalts binder stored for 4 months at room temperature became lower than that of the one fresh prepared with different added contents of SBS-g-M as shown in Fig. 3. It means that a little part of SBS-g-M accumulated at the surface of binder when stored for long time in our situation, which needs to improve further more (see Fig. 4).

Table 2
Effect of SBS-g-M on SHRP specification

Mass fraction of modified asphalt (%)	$T_{SHRP}/^{\circ}\text{C}$ ($G_{ast}^*/\sin \delta = 1 \text{ kPa}$)
0	67.5
3.0%	75.0
6.0%	80.5
8.0%	82.1

Table 3
The isolation degree of PMA measured before and after stored for 4 months

Samples	Softening point upper part/ $^{\circ}\text{C}$	Softening point below part/ $^{\circ}\text{C}$	The temperature gap between upper and below part/ $^{\circ}\text{C}$
1#(A)	53.2	51.7	1.5
1#(B)	54.8	52.5	2.3
2#(A)	60.6	60.4	0.2
2#(B)	62.6	61.4	1.2

A: Fresh blending; B: Stored 4 months.

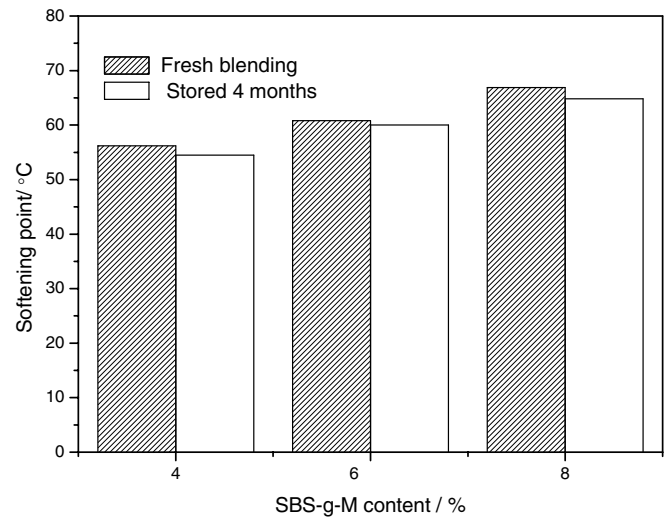


Fig. 3. Effect of SBS-g-M content on softening point of modified asphalt binder.

3.4. Polymer phase morphology

The morphology of PMA was usually investigated by use of fluorescence microscope to characterize the distribution and the fineness of polymer dispersed in the asphalt matrix. Fig. 5 showed the micrographs of the SBS-modified asphalts binder coated on a thin slide, in which the yellow vision was came from SBS and the black vision was came from asphalt. Obviously, SBS is difficult to disperse into asphalt binder with addition of 6% SBS even under high shear stress and at high temperature of 170 °C as shown in A. With the store time from 30 min to 60 min at 160 °C [Fig. 5(B) and (C)] the accumulated particle size of SBS increased gradually. So a lot of companies improved the blending process with addition of some stabilizing agents in preparation of PMA binder with SBS. With stored time, which indicates that the polystyrene domain of SBS, which acts as a receiving unit for stabilization of the dispersed SBS particles, was dispersed finely throughout the asphalt while without being stabilized in the asphalt matrix.

In situation with 6% SBS-g-M the micrograph of the PMA binder was shown in Fig. 6(A), its particle size became very small and SBS-g-M dispersed in the asphalt matrix very homogeneously under the same high shear stress and at the same high temperature. As shown in Fig. 6(B) and 6(C) along with the stored time from 1 h to 24 h at 160 °C the particle size became much smaller and SBS-g-M dispersed more homogeneous, which implied that the SBS-g-M modified asphalt binder had high temperature storage stability. Because of its polarity it is reasonable that SBS-g-M has significant compatibility with base asphalt and can keep binder more stable stored at high temperature within 24 h and more than 4 months at room temperature.

The binder rheological properties and morphology are the result of the inter-effect of polymer and asphalt, composition, nature and content of added polymer [17]. So the

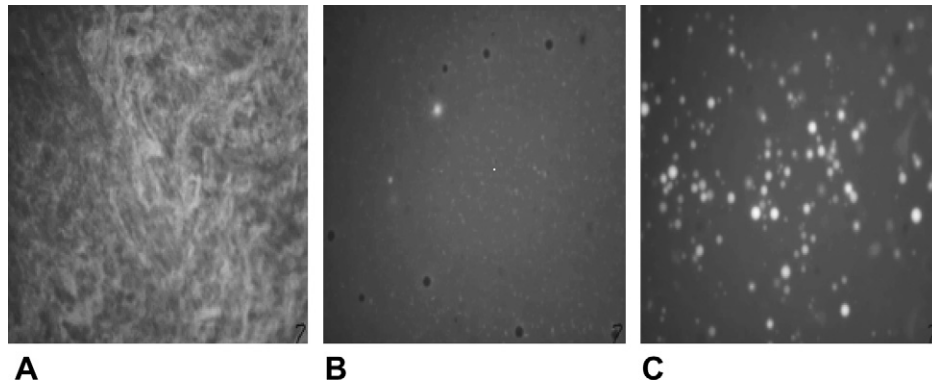


Fig. 4. Phase structure of modified asphalt with 6% SBS-g-M before and after storage 4 months observed by fluorescence microscope with a magnification of 100 \times at room temperature. (A) Fresh blending. (B) Bottom section of the tube after 4 months stored at room temperature. (C) Top section of the tube after 4 months stored at room temperature.

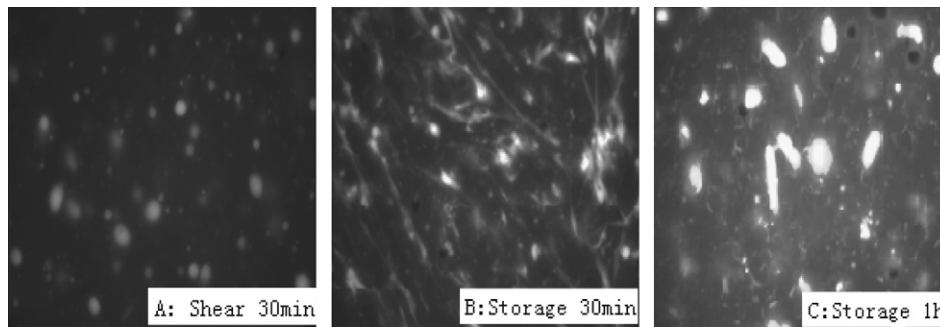


Fig. 5. Fluorescence micrographs of modified asphalt binder with 6% SBS.

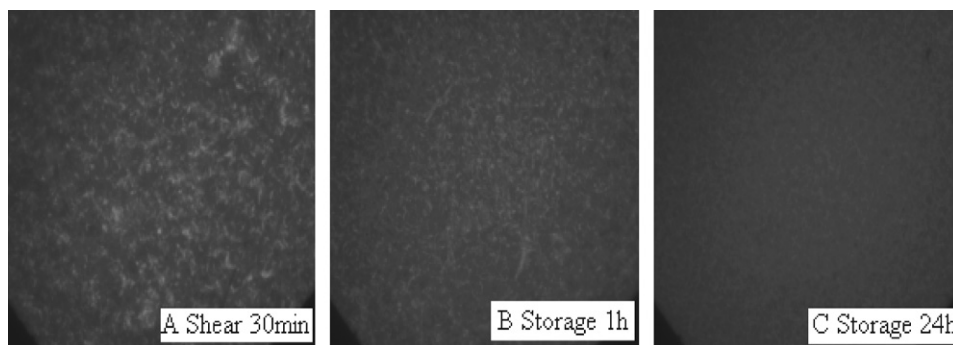


Fig. 6. Fluorescence micrographs of modified asphalt binder with 6% SBS-g-M.

compatibility between polymer and asphalt is critical to the properties of PMAs [16,18]. When SBS is added to asphalt, it absorbs part of its fraction (i.e. saturates and naphthene aromatics) and can be extended and dispersed in asphalt. Consequently, SBS-modified asphalt binder is a multiphase system formed with a polymer-rich phase and an asphalt-rich phase [19]. The SBS builds a three-dimensional network in the polymer-rich phase with the swollen polystyrene end-blocks acting as physical cross-links, which may be perfect when SBS-g-M was added in binder.

4. Conclusions

Storage-stable SBS-g-M-modified asphalt binder has been successfully prepared with addition of polar monomer grafted SBS in γ -rays irradiation method. The characteristics of asphalt/SBS-g-M binder determined by an ARES strain-controlled rheometer can be used to check the ultimate properties of binders used in road pavement. The physical properties of SBS-g-M modified asphalt including softening point, isolation degree and morphology, stored at

high temperature and room temperature in different stored time, are also important for judgment on the compatibility between polymer and asphalt. It has been found that addition of SBS-g-M will bring more obvious improvement to binder as blended system may form more perfect network in modified asphalt binder, which makes binder have advantage in high temperature performance and reduce its temperature susceptibility. Direct Morphology observation by use of fluorescence microscope is very useful to confirm the compatibility and storage stability of SBS-modified asphalt binder.

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