



Rheology and thermal stability of polymer modified bitumen with coexistence of amorphous phase and crystalline phase

Tian Xia^{a,*}, Longmei Zhou^a, Jianhui Xu^{b,c}, Yaping Qin^a, Wenqiang Chen^a, Jianfeng Dai^{a,c}

^a College of Material Science and Engineering, Chongqing University of Technology, Chongqing 400054, China

^b College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, China

^c China Merchants Chongqing Communications Technology Research and Design Institute, Chongqing 400067, China

HIGHLIGHTS

- Coexistence of crystalline phase and amorphous phase lead to a variety of phase structure in polymer modified bitumen.
- Wavelike oscillation phenomenon is liable to happen in the ternary bitumen/SBS/crystalline polymer systems.
- The addition of crystalline polymer into bitumen/SBS can improve the thermal stability.

ARTICLE INFO

Article history:

Received 28 November 2017

Received in revised form 7 May 2018

Accepted 7 May 2018

Keywords:

Stability
Rheology
Crystalline
Amorphous
Modified bitumen

ABSTRACT

The addition of crystalline polymer into bitumen/SBS blends makes an effect on the phase structure, rheological property and thermal stability. The thermal stability measured by DSC can be improved by the crystalline polymer below 100 °C which is lower than the melting point of single crystalline polymer. Complex modulus and phase angle results suggest that the bitumen/SBS/crystalline polymer blends have much better rheological property rather than the bitumen/SBS blend when the SBS fraction keeps the same in both ternary and binary blends. Among PE, PP, and POM three crystalline polymers, PE is the best candidate for the modification of SBS/bitumen blends. The influence of phase structure on the rheological behavior is investigated, regarding the phase structure type, droplet size and the crystalline or amorphous property.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

With the increasing traffic load, higher traffic volume, and insufficient maintenance, the pavement surface is liable to experience severe diseases such as rutting or cracking [1]. The harsh reality is the main reason for the improving quality of bitumen material, especially the polymer modified bitumen. As the most popular thermoplastic elastomer, styrene–butadiene–styrene (SBS) triblock copolymer presented the best results in improving the bitumen properties [2,3]. SBS has a two-phase morphology of spherical PS block domains within a matrix of PB. Between the glass transition temperatures of PS blocks (~100 °C) and PB blocks (~–90 °C), PS behaves as glassy while PB behaves as rubbery, giving rise to both strength and elasticity of SBS and the possibility of physical crosslink formation [4].

* Corresponding author.

E-mail address: xiatian@cqut.edu.cn (T. Xia).

Phase separation in SBS modified bitumen (SMB) is the main concern in the field of bituminous pavement construction since it would result in a stratification in their blend. The original reason for this phase separation is the competition between SBS and asphaltenes to absorb the insufficient light components of bitumen. Our recent study [5] found that there was a pronounced contrast in complex modulus G^* and complex viscosity η^* contrast between SBS and bitumen, implying a large dynamic asymmetry in their blends. This contrast provides the prerequisite of viscoelastic phase separation occurrence, during which a transient network structure can be formed [6,7]. Usually, the phase structure can directly influence the service performance of SBS modified bitumen, which can be revealed by rheology, for example, the G^* is an indication of rutting resistance. It is easy to understand that the service performance of SBS modified bitumen improves with the increase of SBS.

Recently, the addition of nanofillers into the bitumen/SBS blends has been attracted much attention due to its extraordinary ability in mechanical property enhancement and cost reduction.

For example, the addition of nanoclay montmorillonite [8,9] or SiO₂ nanoparticles [10] into bitumen/SBS could lead to a remarkable enhancement in modulus, rutting resistance. The inorganic fillers are one of the best candidate for a further modification of bitumen/SBS blends due to its rigidity. However, it is difficult to make them well dispersed in the viscous blends by melt-mixing method especially when the fillers are nanoscale with high specific surface area. Under this situation, the nanofillers tend to assemble each other into larger size aggregates. Meanwhile, the random distribution of nanoparticles and their aggregates would make the bituminous material heterogeneous and weaken its service performance.

The above discussion suggests that, there may be another route to produce a polymer modified bitumen with good service performance while its prepared method can be available for engineering production. Regarding this, we used different crystalline polymers instead of nanofillers into the bitumen/SBS blends and compared their rheological property and phase structure in this study. As a ternary blend, the phase structure may be complex due to the multiple compatibility among bitumen, SBS and the crystalline polymer. Usually, crystalline polymer has high rigidity, tensile strength and tensile modulus while SBS can provide the material toughness and elasticity. If they can keep their individual advantage in the ternary bituminous materials, it will provide another efficient and convenient way of bitumen modification.

2. Materials and experiments

2.1. Materials and sample preparation

Bitumen (AH-70#) used in this paper was provided SK company in 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 TLC-FID [5,11]. SBS (1301) was supplied by Yueyang Baling Company, Sinopec, which was a linear structure polymer containing 30% styrene by weight with M_w of 10^5 g/mol. Polyethylene (PE), Polypropylene (PP), and Polyoxymethylene (POM) are chosen to be the crystalline polymer modifiers. PE (DMDA-8008) with a melt flow index (MFI) of 7.3 g/10 min and density of 1.047 g/cm³ was obtained from Dushanzi Petrochemical Corp [12]. PP (Z30S) were obtained from Taiwan Polypropylene Co. Ltd (Taiwan) with a MFI of 25 g/10 min and a density of 0.9 g/cm³ [13]. POM (M90) was provided by Yun-Tian-Hua Co. Ltd with a MFI of 9.0 ± 1.20 g/10 min and a density of 1.4 g/cm³ [14].

The base bitumen was heated in an iron container. The temperature kept invariable at 190 °C, and SBS (or SBS/crystalline polymer) were added to the bitumen in a stirring machine for 30 min. After that the mixing was continued at that temperature using a high shear mixer with 3000 rpm for 1 h under 190 °C. For binary blends, the SBS fractions were 4 wt%, 5 wt% and 6 wt% of bitumen. For ternary blends, the SBS fraction is kept as 4 wt% of bitumen while the crystalline polymer fraction is 2 wt% of bitumen. The binary SBS modified bitumen was abbreviated as SMBX that X denotes the fraction of SBS in bitumen by weight. The ternary bitumen/SBS/crystalline (100/4/2) blends were abbreviated as SMB/Y that Y denotes the crystalline polymer.

2.2. Experiments

Thermal characteristics of materials were investigated by a differential scanning calorimeter (DSC Q20, TA Instruments). Samples weighing about 4–10 mg sliced from compressed specimens were examined. During scanning, the samples were protected under a nitrogen flow of 50 ml/min. Three kinds of test procedures were employed. (i) Melting point measurement. For this measurement, single crystalline polymer was loaded in temperature range from 50 °C to 250 °C with a scanning rate of 15 °C/min. After the first heating scanning to 250 °C, it was annealed for 3 min to eliminate the heat history. Then it was cooled down to 50 °C, and finally heated again to 250 °C. The final melting process result was given in Fig. 1. (ii) Thermal stability measurement for polymer modified bitumen. The tested temperature range is –50–200 °C for the blends and single SBS, –20–100 °C for base bitumen. The heating rate is still 15 °C/min. (iii) Time sweep test of polymer modified bitumen at 60 °C for 60 min.

Rheological test was performed on a rheometer (AR 1500ex, TA Instruments, USA) with 25 mm parallel plate and 1 mm gap geometry. Three oscillating mode tests were employed as follows: (i) Frequency sweep test, which was carried out at 60 °C with a sweep frequency range of 100–0.01 rad/s. (ii) Time sweep test, which was measured at 60 °C, three fixed frequencies were selected as 1 rad/s,

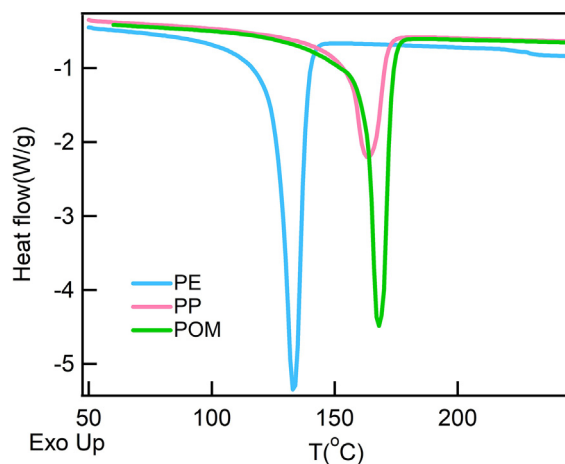


Fig. 1. DSC curves of heating process from 50 °C to 250 °C for single crystalline polymers.

5 rad/s and 10 rad/s, each sweep step lasted for 40 min. For each rheological test, the strain was kept as 1% which was low enough to ensure the location of linear viscoelastic region.

Optical microscopy was used to study the phase structure of polymer modified bitumen. A drop of a heated sample was placed between the microscope slides. Samples were observed using an optical microscope (BK-POL-TR) from Optec Company in China under transmission mode and polarization mode.

3. Results and discussion

It can be seen in Fig. 1 that a clear endothermic peak appears on the heating curve due to melting of polymer crystal. The T_m at peak position of PE, PP and POM are 134 °C, 163 °C and 168 °C, respectively.

As Fig. 2(a) shows, the base bitumen experiences a glass transition during –20 °C to 20 °C and then exhibits an endothermic peak subsequently. This is related to the amorphous–crystal transition of the n-alkane paraffinic material in bitumen. Once entering T_g region, the methylene carbon segments of the n-alkane molecules have sufficient mobility to rearrange to an all-trans conformation, leading to the cold crystallization occurrence [15]. As for SBS, there is a glass transition around in the range of 59 °C to 79 °C, close to the value of SBS R4555 with S/B of 55/45 reported by Lackner. R et.al [16].

Since the complex structure of bitumen and the phase structure induced by the compatibility between polymer and bitumen, the modified blends are unstable during the heating process. For each blend, the fluctuation is relatively weaker before the temperature reaches 100 °C in Fig. 3. An endothermic peak also can be observed for each bitumen/SBS/crystalline polymer blends. The T_m (melting point) at peak position for SMB/PE, SMB/PP and SMB/POM are 122 °C, 158 °C and 162 °C, lower than that of the corresponding single crystalline polymer. This T_m decrease result may be influenced by the interaction between bitumen and semi-crystalline polymer. The semi-crystalline polymer molecular chains can gain strong mobility since it would be partially swollen by some light aromatic components of the bitumen [17]. Accordingly, the melting point of crystalline polymer in the blends is reduced due to its better flexibility. It is worth noting that there is an exothermic peak around 135 °C for all the blends except SMB/PE. As indicated by Fig. 8, the phase structures measured by optical microscopy indicate that, all the studied systems experience phase separation, including SMB6, SMB/PP, SMB/POM as well as SMB/PE blends. Thus, the exothermic peak emerged in the former three blends reflects the phase separation occurrence. The disappearance of exothermic peak in SMB/PE blend suggests that the phase separation process

Download English Version:

<https://daneshyari.com/en/article/6712833>

Download Persian Version:

<https://daneshyari.com/article/6712833>

[Daneshyari.com](https://daneshyari.com)