Rheological stability enhancement of polyethylene modified bitumen by the addition of paraffin wax

T Xia¹, X Chen¹, J H Xu¹,²*, J F Dai¹,² and Y Y Li²

¹College of Material Science and Engineering, Chongqing University of Technology, Chongqing, China.
²Chongqing Zhixiang Paving Technology Engineering Co., Ltd., China Merchants Chongqing Communications Technology Research and Design Institute, Chongqing, 401336, China.

Email: xujianhui@cmhk.com

Abstract. The rheological behavior of Polyethylene (PE) modified bitumen is investigated. It is found that a rheological plateau under high temperature presented on the curve of storage modulus (\(G^*\)) variation with temperature. By the addition of little wax, the rutting resistance of bitumen/PE blend can be further improved. Moreover, the wax incorporation into bitumen/PE can significantly decrease the starting temperature of rheological plateau to accommodate the actual service temperature of bituminous pavement, making a potential application of PE/wax modified bitumen in pavement engineering. The reason for this rheological property enhancement by wax is explored in terms of phase separation structure and thermal behavior of bitumen/PE blends. Main focus is put on the relationship between PE crystallinity and rheological behavior.

1. Introduction

With the intensification of global warming, bituminous materials are susceptible to form rutting especially in summer. At the same time, the heavy traffic loads and large volume of vehicles accelerate the rutting formation, and consequently reduce the service life time of bituminous pavement. As a popular bitumen modifier, polyethylene (PE) can significantly enhance bitumen’s rutting resistance [1]. The reason for the good ability of PE to resist rutting of bitumen is related to its molecular structure, which has two hydrogen atoms attaching on each carbon. Such regular and symmetric structure make it prone to crystallize. High crystallinity can endow PE high rigidity, and its addition into bitumen could result in a substantial reduction of deformation under traffic loads. Consequently, PE modified bitumen displays an extraordinary rutting resistance [2]. Moreover, the addition of PE into bitumen also improves its fatigue resistance and reduces its temperature susceptibility [3].

However, various disadvantages of the PE-modified bitumen should not be neglected. One of the main issues is the pronounced difficulty of dissolving the PE particles in hot bitumen due to the intrinsic nonpolar and nonaromatic nature of PE [4,5]. The other is phase separation between PE and bitumen due a density difference and weak compatibility between them, especially when the modified bitumen is stored at high temperatures without constant stirring [6-9]. In fact, phase separation is the result of competition between polymer chains and asphaltenes in bitumen to absorb the insufficient light components [10]. It is reported that [11,12] the addition of reactive polymers containing functional groups suitable to react with specific bitumen molecules can solve the storage instability of PMB...
mentioned above. For example, using the maleic anhydride grafted polyethylene and the premixing of nanoclay with polyethylene phase led to improved dispersion state of nanoclay in polyethylene modified bitumen nanocomposites [13]. Usually, better compatibility or miscibility between polymer and bitumen may enhance its rheological property, such as complex modulus improvement. Our recent studies [14,15] found that once a network structure can be formed by viscoelastic phase separation, the rheological property of modified bitumen can also be significantly improved. Moreover, it is found that a plateau in the range of 80–120 °C is present on complex modulus ~ temperature (\(G^*\sim T\)) curve of bitumen/PE/saturates–butadiene–styrene (SBS) blend, revealing a rheological stability. In other words, the temperature susceptibility of bitumen can be relieved by adding PE/SBS blend. The reason for this plateau formation is the crystalline PE-rich network with high stiffness. If the starting temperature for the \(G^*\sim T\) plateau can be lowered to accommodate the actual service temperature of bituminous pavement, it will attract much attention in both scientific and engineering application.

In this work, another crystalline component (paraffin wax) with low melting temperature is employed into bitumen/PE blends to regulate the rheologically stable temperature range. The PE/paraffin wax blend is reported as a phase change material in which paraffin acts as a dispersed phase for low-temperature heat storage and PE acts as a supporting material [16]. However, the study on the PE/paraffin wax modified bitumen has attracted little attention. This work would provide an easy way to prepare polymer modified bitumen with rheological stability. Corresponding mechanism is explored by their crystallization behavior and phase separation structure.

2. Materials and Experiments

2.1. Materials and sample preparation

Bitumen (AH-70#) was supplied by SK company in Korea, the content of saturates, aromatics, resins and asphaltenes are 5.9%, 59.8%, 19.1% and 15.2% respectively, measured by TLC-FID. High density polyethylene (HDPE) with grade of DMDA-8008 was provided by Dushanzi Petrochemical Corp [17]. The melt flow index (MFI) and density of HDPE were 7.3 g/10min and 1.047 g/cm³, respectively. Paraffin wax (n-alkane) was provided by Hualing rehabilitation machinery factory, Shanghai, China.

The polymer modified bitumen was prepared by melt blending method. At first, the base bitumen was heated at 180 °C until it exhibits a flow state. Then polymers were added together into the bitumen with a high shear mixer with 5000 rpm for 2 h under 180 °C. The binary bitumen/PE (100/10) by weight blend was regarded as neat sample which was abbreviated as BE, and it compared with bitumen/PE/wax (100/10/2) by weight which was abbreviated as BEX to study the influence of wax on its rheology and microstructure.

2.2. Experiments

Rheological test was performed on a rheometer (AR 1500ex, TA Instruments, USA) with 25 mm parallel plate and 1 mm gap. A dynamic temperature ramp step was tested from 25 °C to 125 °C with heating rate of 1 °C/min at a fixed frequency of 10 rad/s. The strain was kept in linear viscoelastic region.

Microscale phase separation structure was observed by optical microscopy equipped with a charge coupled device camera and a hot stage. The optical microscopy (BK-POL-TR) is supplied by Optec company, China. Sample for structure observation is prepared by a melting cast method of bituminous sample.

The thermal behavior of samples was measured by DSC (Q20, TA Instruments, USA). Samples about 4–10 mg were picked up from modified bitumen. The whole scanning process was protected under a nitrogen flow of 50 ml/min. Temperature sweep of polymer modified bitumen is heated from 25 °C to 180 °C with 10 °C/min increment. As for bulk PE, it was firstly heated from 40 °C to 200 °C with heating rate of 10 °C/min, and then kept isothermal for 3 min to eliminate the thermal history. After that, it was cooled down to 40 °C with heating rate of 10 °C/min for crystallization. Finally, it was heated again to
200 °C with heating rate of 10 °C/min. DSC measurement for bulk was is similar to that of bulk PE, just the temperature ramp changed as −60 °C to 100 °C.

3. Results and discussion
The temperature ramp test results of polymer modified bitumen measured by rheology were displayed in Figure 1. It is obvious that both $G'$ for BE and BEX decrease with temperature, which indicates the greater mobility of molecular chains at higher temperature [18].

Once the temperature exceeds a critical value as the arrow indicates, a plateau-like shape shows on $G' \sim T$ curve. The temperatures for the starting temperature ($T_s$) for the plateau are 78 °C and 62 °C for BE and BEX, respectively. This $T_s$ reduction suggests that the addition of wax can effectively regulate the rheologically stable temperature of bitumen/PE blends.

When $T < T_s$, the $G'$ value of BE and BEX are almost overlapped. Once the temperature exceeds $T_s$, $G'$ decreases very slowly with temperature and seemingly reaches a plateau value. There is a distinguished difference in $G'$ between BE and BEX in the plateau temperature range, and the $G'$ of BEX is much higher than that of BE. This result implies an enhancement of rutting resistance at high temperature after the addition of wax into bitumen/PE blends. Combined $T_s$ reduction and $G'$ improvement phenomenon, it can be known that the incorporation of wax into bitumen/PE blends can effectively weaken its high temperature susceptibility.

Figure 1. Complex modulus $G'$ variation with temperature $T$ of BE and BEX.

Figure 2. Tan δ variation with temperature for BE and BEX.

Figure 3. SHRP temperature comparison between BE and BEX.
In fact, besides the $G'$ improvement, the elasticity of bituminous material also be enhanced by the addition of wax, which is reflected by tan $\delta$ in Figure 2. An obvious broad peak presents on each tan $\delta$ curve, indicating the existence of network structure in the blends [19]. The peak temperature derived from tan $\delta$~$T$ curves are 54 and 44 °C for BE and BEX, respectively. When the temperature is higher than ~40 °C, the tan $\delta$ value of BEX is obviously lower than that of BE, indicating the much more elasticity of bitumen/PE after the addition of wax.

Moreover, there is a large contrast of SHRP (Strategic Highway Research Program) temperature between BE and BEX as displayed in Figure 3. SHRP temperature is defined as the highest temperature when $G'/\sin \delta$ is more than 1 kPa [9]. The SHRP temperature is ~60 °C for BE but ~120 °C for BEX, showing a significant enhancement of rutting resistance of bitumen/PE blends after the addition of wax.

The property of material is directly related to its microstructure. The phase structure of BE and BEX are displayed in Figure 4. Both of them form a typical network structure, which is induced by viscoelastic phase separation between bitumen and PE [15]. As we know, the crystalline with spherulites under polarization can be displayed as a cross extinction frame [20], but the amorphous bitumen or wax can not be visible under polarization mode. Thus, we used optical microscopy with both transmission and polarization modes to distinguish the PE-rich phase. From Figure 4, the network still can be clearly observed in Figure 4(a'-b'), indicating that it is mainly composed of PE-rich phase while the dark region should be bitumen-rich phase. The existence of crystalline PE network with high stiffness can be the reason for the presence of plateau of $G'$~$T$ curve and the broad peak of tan $\delta$~$T$ curve, since its crosslinks can effectively resist the deformation when the bituminous material is subjected to external force.

It is noticed that from Figure 4(b) and (b'), we can not distinguish the crystalline PE-rich phase and wax-rich phase. This result reflects the rather miscibility between PE and wax, due to the hydrophobic and crystalline nature of them. The wax would prefer to disperse in PE-rich phase rather than in bitumen-rich, and their crystallization processes also interplay with each other. Consequently, the crystalline morphology of PE-rich phase and wax-rich phase form into a continuous network phase.

Since the crystalline PE with high stiffness plays a main role in the rutting resistance of bituminous material, the possible reason for $G'$ improvement under high temperature may be related to positive contribution of wax to the crystallinity of PE. Thus, thermal behavior of polymer modified bitumen should be studied.
As shown in Figure 5, the crystallization temperature at exotherm peak is ~115.6 °C for bulk PE, and its corresponding endotherm peak is located at ~133 °C. Different from bulk PE, there are two crystallization peaks at ~53 °C and ~36 °C for bulk wax. The corresponding melting endotherm peaks for bulk wax are around ~58 °C and ~40 °C, respectively.

![Figure 5. DSC curves of (a) cooling process and (b) heating process for bulk polymers.](image)

Based on the above differential scanning calorimeter (DSC) result of bulk polymers, both PE and wax should be crystallized during cooling down from hot mix temperature to room temperature. However, there is only one endotherm peak located at the ~123 °C for BE and BEX as shown in Figure 6. This temperature corresponds to the melting temperature of PE in bitumen [15], above which the crystalline PE would turn into totally flow state and resulting in a failure of bituminous material.

![Figure 6. DSC curves of heating process for polymer modified bitumen.](image)

The disappearance of wax endotherm peak on DSC curve of BEX may be due to its minor fraction (only 2wt.%) of base bitumen. The melting endotherm ($\Delta H_m$) value for crystalline-to-amorphous transition of PE for BE and BEX can be calculated as 15.5 J/g and 19.4 J/g respectively in the range of 100–140 °C. Noticed that 100–140 °C range is selected without any strict definition, just for the endotherm comparison between BE and BEX to ensure them within the same temperature range. It should be noted that three DSC replicates were performed and the heat flow values are averaged by the three similar tested data. Thus, the difference in $\Delta H_m$ value should not be ascribed to experimental data fluctuation.
The $\Delta H_m$ of polyethylene with 100% crystallization ($\Delta H_{100}$) is 293 J/g [21]. Thus, the crystallinity ($X_c$) of PE in BEGs can be calculated as the following equation, in which $x_m$ is the weight fraction of PE in modified bitumen.

$$X_c = \frac{\Delta H_m}{\Delta H_{100} \times x_m} \times 100\%$$

Based on the above equation, the $X_c$ (PE) of BE and BEX are calculated as 54.9% and 74.2%, respectively. This significant improvement of PE crystallinity induced by the addition of wax makes PE-rich network much stiffer, resulting in rheological stability enhancement as revealed by Figure 1.

4. Conclusions

It is found that small amount of crystalline wax can effectively enhance the rutting resistance of PE modified bitumen. The SHRP temperature can increased from ~60°C to ~120°C, which is close to melting temperature of crystalline PE. Phase structure observed by optical microscopy exhibits a typical network structure for both BE and BEX induced by viscoelastic phase separation. The network structure with lots of crosslinks can effectively resist the deformation, leading to a plateau-like shape on $G^*$ ~ $T$ curve for both BE and BEX. This is also an indication of rheological stability under high temperature. The original reason for this result is the improved crystallinity of PE by the addition of wax, which makes PE-rich network much stiffer, and accordingly endows the modified bitumen stronger rheological stability.

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