Research Article

Effect of Warm-Mix Agent EC-120 on Performance of Asphalt Binder and Its Microscopic Mechanism

Tian Xiaoge, Ren Zhang, Yichao Xv, Yantian Chu, Zhen Yang, and Shaohua Zhen

School of Traffic & Transportation Engineering, Changsha University of Science & Technology, Changsha, Hunan 410114, China

Correspondence should be addressed to Tian Xiaoge; tianxiaoge@126.com

Received 13 December 2018; Accepted 26 February 2019; Published 14 March 2019

Academic Editor: Hao Wang

Copyright © 2019 Tian Xiaoge et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In order to figure out the influence of the warm-mix agent EC-120 on the performance of the asphalt binder and its micro mechanism in warm-mixing process, a matrix asphalt, A-70, and SBS-modified asphalt, SBS I-D, were modified with different contents of EC-120, respectively. Then, conventional macromechanic performance tests, dynamic shear rheological (DSR) test at high-temperature, and bending beam rheological (BBR) test at low-temperature were carried out on asphalt binder samples. Meanwhile, they were microscopically analyzed through Fourier transform infrared spectrometer (FTIR) and differential scanning calorimeter (DSC). The results indicated that EC-120 can reduce the viscosity of asphalt binder at high temperature. With the increase of EC-120 content, the high-temperature rutting resistance of two kinds of warm-mix asphalt (WMA) increased, but their crack resistance at low-temperature was reduced. FTIR indicated that this is due to the generation of oxides containing carbonyl functional groups after EC-120 was blended with asphalt binder. The DSC endothermic curves of WMA binders are obviously different from those of base binders, and a strong endothermic peak appears in the interval of 102°C–113°C, indicating that EC-120 will endothermically melt at the temperature of 102°C–113°C, so it can play the role in reducing the viscosity of asphalt binder at the range of construction temperatures.

1. Introduction

Warm-mix asphalt (WMA) refers to the use of certain technical means in the mixing process of asphalt mixture, which can effectively reduce the construction temperatures of the mixture in mixing, spreading, and rolling processes and assure the performance of the mixture not lower than that of hot mix asphalt (HMA) [1–3]. The mixing temperature of WMA is generally 100°C–120°C, and the paving and compacting temperature is about 80°C–90°C. Compared with HMA, the construction temperatures are reduced about 30°C, but it has the same workability and performance as HMA [4]. A large number of researches and practices have shown that WMA mixture has the characteristics of good performance, low emission, and low energy consumption compared with HMA mixture [4–6]. As an energy-saving green material, WMA is receiving more and more attention in pavement engineering [7].

In the early stage of WMA researches, most of them focused on conventional problems such as construction temperature, gradation design, and pavement performance, which are practical problems in the application of WMA technology [5, 7]. Rodriguez-Alloza et al. comparatively studied the mechanical properties of WMA with different warm-mix agents [8]. Buss et al. [9], Chomicz-Kowalska et al. [10], and Cucalon et al. [11] studied the effect of warm-mix agent on the moisture susceptibility of asphalt mixture. Podolsky et al. studied the rutting resistances of WMAs [12].

In recent years, research on WMA has been deepened. Advanced microscopic testing techniques have been used to study the effects of warm-mix agents at a microscopic scale. Menapace et al. studied the surface morphology of WMA at different UV aging stages with optical microscope and atomic force microscope (AFM) [13]. Nazzal et al. examined the moisture susceptibility and healing characteristics of WMA and compared it with those of conventional HMA with the atomic force microscopy (AFM) [14, 15]. Hossain et al. evaluated the effects of two WMA additives on the chemical compositions of asphalt binder with spectroscopy techniques including Fourier transform infrared (FTIR)
spectroscopy, nuclear magnetic resonance (NMR), and X-ray photo electron spectroscopy (XPS) [16]. Abd et al. studied nanoscale properties of WMA with atomic force microscopy [17].

The object of this paper is to evaluate the effect of warm-mix agent, EC-120, on the performance of WMA, so the DSR tests and BBR tests were adopted to evaluate the effect of EC-120 on the macroperformance of asphalt binder. FTIR and DSC tests were adopted to analyzed its warm-mixing mechanism from a microscopic view.

2. Raw Materials and Test Methods

2.1. Raw Materials

2.1.1. Asphalt Binder. Two kinds of asphalt binder, ESSO A-70 matrix asphalt provided by Taihe Asphalt Products Co., Ltd. and a finished SBS modified asphalt, SBS I-D, provided by Zhenjiang Asphalt Co., Ltd. were utilized. The main technical indexes are shown in Tables 1 and 2, respectively [18–20].

2.1.2. Warm-Mix Agent, EC-120. EC-120 is an organic viscosity reducing asphalt modifier developed by Haichuan Company. It is a long-chain aliphatic polymer. It is in the form of tiny round particles at room temperature. The technical indexes are shown in Table 3.

2.2. Experiment Methods. To evaluate the effect of EC-120 on macro performance of asphalt binder, different contents of EC-120 (0%, 1%, 2%, 3%, 4%, 5%), were mixed with A-70 and SBS I-D, respectively.

Asphalt binders were placed into ovens at different constant temperatures (150°C for A-70 and 170°C for SBS I-D) for 1 hour to melt them. Then they were taken out and weighed for the required binder and mixed with different weights of EC-120. They were mixed with high-speed shear mixer. The mixing speed is 5000rpm. The temperature was kept at 140°C (A-70) or 160°C degrees (SBS I-D) during mixing. After mixing for 30 minutes, they were put into an oven of 140°C or 170°C for 30 minutes to make them fully swollen.

Six groups of warm-mixed A-70 samples and six groups of warm-mixed SBS I-D samples were prepared. The binder with 0% EC-120 is the base binder, and the others are WMA binders. The following macroscopic performance tests and microscopic measurements were then conducted on these samples:

(1) Dynamic shear rheometer (DSR) test [21] at high temperature: MCR301 produced in Germany was adopted. The diameter of plates is 25 mm, and the height of binder samples, the gap between rotating plate and fixed plate, is 1 mm. The value of loading strain was controlled to 12%. The loading frequency was set to 10 rad/s. Test temperatures were set at 52°C, 58°C, 64°C, and 70°C. The rutting factor, $G^′/sin \delta$, calculated through the collected data of complex shear modulus, $G^′$, and phase angle, $\delta$, was adopted to characterize the high-temperature performance of base binder and WMA binder.

(2) Bending Beam Rheometer (BBR) tests [21] at low-temperature: BBR-TE produced in the United States was adopted. The width of the beam is 12.5 mm, the height is 6.25mm, and the distance between the supports is 102 mm. Constant load applied is 988 mN. Test temperatures were set at $−12°C$, $−18°C$, or $−24°C$ respectively. The stiffness modulus, $S$, and creep rate, $m$, were calculated to characterize the low-temperature crack resistance of base binder and WMA binder.

(3) Fourier transform infrared spectroscopy (FTIR): FTIR, as an important way to study the molecular structure of materials, has been widely used in various fields in recent years. By irradiating the sample with infrared light and recording the transmittance of the sample to different wavelengths of infrared light, the corresponding infrared spectrum of the sample can be obtained. The molecular composition of the sample can be determined through comparing the spectrum and the fingerprint area [22]. TENSOR27 infrared spectrometer

---

### Table 1: Technical indexes of ESSO A-70 matrix asphalt.

| Technical indexes | Unit       | Results | Specification |
|-------------------|------------|---------|---------------|
| Penetration       | mm         | 0.94    | 0.10          |
| Softening point   | °C         | 47.5    | 47            |
| Ductility @15°C   | cm         | >100    | ≥100          |
| Relative density  | %          | 1.043   | Measured      |
| After TFOT        | %          | 0.1     | ±0.8          |
| Mass changes      | %          | 65.2    | ≥63           |
| Residual penetration ratio | %      | 70.1    | ≥65           |
| Residual ductility | cm    | 28.4    | ≥15           |

### Table 2: Technical index of SBS I-D modified asphalt.

| Technical index | Unit       | Results | Specification |
|-----------------|------------|---------|---------------|
| Penetration     | mm         | 0.1      | 0.1           |
| Softening point | °C         | 83.4     | 70            |
| Ductility @5°C  | cm         | 35.0     | ≥25           |
| Relative density @25°C | 1.027 | Measured | |
| After TFOT      | %          | −0.422   | ±1.0          |
| Mass changes    | %          | 70.1     | ≥65           |
| Residual penetration ratio | %      | 70.1    | ≥65           |
| Residual ductility | (5°C, 5 cm/min) | 28.4    | ≥15           |

### Table 3: Technical indexes of EC-120.

| Index | Viscosity @135°C (cp) | Penetration @25°C (0.1 mm) | Density @25°C (g/cm³) | Freezing point (°C) | Flash point (°C) |
|-------|-----------------------|----------------------------|-----------------------|---------------------|------------------|
| Typical values | 12                | <1                          | 0.94                  | 100                 | 290              |
produced by BRUKER company was used to analyze the changes of molecular composition in the two kinds of asphalt binder, A-70 and SBS I-D, before and after added EC-120, so as to study the warm-mixing mechanism of EC-120 on asphalt binder from the molecular perspective.

Asphalt samples were prepared through thin filming method. 1.0 gram of asphalt binder was added into 10 ml of carbon tetrachloride solution, when asphalt binder was completely dissolved, and solution was dropped onto the potassium bromide window sheet and dried under a electric heated lamp. So, a film sample of asphalt binder required for FTIR experiment was prepared.

The pressing plate method was used for EC-120 sample preparation because it is a kind of granular solid. EC-120 and potassium bromide powder were mixed at a mass ratio of 1:100 and then pressed into a sheet by a hydraulic machine.

(4) Differential scanning calorimetry (DSC): Different materials have different thermal effects, so the thermal effects of materials can be utilized to analyze its composition. The peak and its corresponding temperature in DSC spectrum (heat flow versus temperature) can be used to analyze the thermal stability of materials. The peak temperature represents the temperature at which the state of the substance in the material was changed. Enthalpy change ($\Delta H$) can be calculated through integrating the area of the peak. In general, material is in the multiphase blending state when temperature is in enthalpy change zone. There are great differences in the microcomposition, which will lead to sudden changes in the physical and chemical properties of the material before and after this interval, which has an adverse effect on its thermal stability. So, the peak and enthalpy change $\Delta H$ can be adopted to characterize the thermal stability of materials [23].

DSC was adopted to evaluate the thermal effects of base binder and WMA binder. And their DSC spectrums were compared to analyze thermal effect of EC-120 on asphalt binder and to clarify the warm-mixing mechanism.

Sample prepare method: 0.1 gram of asphalt binder was randomly dipped in the melt asphalt binder with a clean pin and then it was adhered into a flat-bottomed aluminum crucible with a capacity of 40 $\mu$l and placed in an oven at 160°C for 15 min until its bottom was evenly covered with asphalt binder. After that, it was placed into the refrigerator for about 10 minutes; at last, it was taken out for DSC test.

Test method: Test temperature was controlled at 20°C to 500°C, temperature rise rate was 10°C/min, the filling gas was inert gas nitrogen, and gas filling rate was 20 ml/min.

According to the DSC spectrum of every sample, three parameters ($T_{m}$: peak value of endothermic, $H_{e}$: peak area of endothermic, and $T_{c}$: melting complete temperature) were calculated. And their variations with dosage of EC-120 were studied to analyze the effect of EC-120.

### 3. Analysis of Test Results

#### 3.1. Effect of EC-120 on High-Temperature Performance of Asphalt Binder

DSR tests were carried out on binders with different EC-120 contents at four different high-temperatures, 52°C, 58°C, 64°C, and 70°C. The rutting factor, $G' / \sin \delta$, of WMAs with different EC-120 contents at different temperatures is shown in Figure 1.

It can be seen from Figure 1 that at the same temperature, the rutting factors of the two types of WMA increased with the increase of EC-120 content, indicating that the addition of EC-120 can improve the rutting resistance of binders. When EC-120 content exceeds 4%, the increase rate of $G' / \sin \delta$ of the two types of WMA is significantly reduced. It can be speculated that a stable grid structure can be formed in asphalt binder when the content of EC-120 is about 4%. The improvement effect of increasing EC-120 content on the high-temperature performance of asphalt is limited when the content of EC-120 is greater than 4%.

#### 3.2. Effect of EC-120 on Low-Temperature Performance of Asphalt Binder

BBR tests were carried out on base binder and different WMA binder samples at different low temperatures of $-12^\circ C$, $-18^\circ C$, and $-24^\circ C$. The creep stiffness modulus, $S$, and creep rate, $m$, were obtained and showed in Figures 2 and 3.

It can be seen from Figures 2 and 3 that with the increase of EC-120 content, the low-temperature stiffness modulus $S$ of the two kinds of WMAs increased and the creep rate $m$ value continuously decreased, indicating that EC-120 has a negative effect on the low-temperature performance of asphalt binder.

### 4. Microscopic Warm-Mixing Mechanism of EC-120

#### 4.1. FTIR Spectroscopy Analysis

FTIR spectroscopy was conducted on EC-120, ESSO A-70 matrix asphalt, SBS I-D modified asphalt, and WMAs; the content of EC-120 were 4% for both ESSO A-70 and SBS I-D. The samples of asphalt binders were prepared through the thin filming method, and the samples of EC-120 were produced through pressing plate method.

The infrared spectrum of EC-120 is shown in Figure 4.

It can be seen from Figure 4 that the peak of EC-120 is between 3250 cm$^{-1}$ and 3700 cm$^{-1}$, and there is a particularly prominent peak at 3500 cm$^{-1}$. This interval is the stretching vibration regions of N-H and O-H. In addition, there are also peaks at 719 cm$^{-1}$ and 1473 cm$^{-1}$, which is caused by -(CH)$_n$-, and the value of $n$ is greater than 4 due to the presence of a peak at 719 cm$^{-1}$. By comparing with the infrared spectrum, the molecular structure of EC-120 is similar to that of polyethylene wax, so it is a kind of PE wax.

The infrared spectra of ESSO A-70 and SBS I-D before and after the addition of EC-120 are shown in Table 4 and Figure 5.
Figure 1: Relationship between $G^*/\sin \delta$ and EC-120 dosage of WMAs. (a) Warm-mixed matrix asphalt A-70. (b) Warm-mixed SBS I-D.

Figure 2: Relationships between $S$ of WMA binders and EC-120 content. (a) Warm-mixed matrix asphalt A-70. (b) Warm-mixed SBS I-D.

Figure 3: Relationships between $m$ of WMA binders and EC-120 content. (a) Warm-mixed matrix asphalt A-70. (b) Warm-mixed SBS I-D.
It can be seen from Table 4 and Figure 5 that due to the addition of EC-120, a new peak presented at 1700 cm$^{-1}$ in the Infrared spectrums of WMA binders, while the other peaks do not change significantly. The peak at 1700 cm$^{-1}$ is a carbonyl group, and the compounds include ketones, aldehydes, carboxylic acids, amides, and acid chlorides. Generally, carbonyl content is very few or nonexistent in unaged asphalt. The aging of asphalt can produce a large number of carbonyl compounds. Therefore, EC-120 chemically reacts with asphalt binder to produce a large amount of oxides containing carbonyl functional groups after blended with original asphalt, which leads to deterioration of its physical properties; this is the reason that WMA binders have better rutting resistance than that of base binder.

### 4.2. Thermal Effect Analysis of EC-120

Differential scanning calorimetry (DSC) tests [24] were conducted on base binder and WMA binder with different EC-120 contents. The test temperature was 60°C to 200°C. The DSC curves of base binders and WMA binders with different EC-120 contents are shown in Figures 6(a) and 6(b), respectively.

It can be seen from Figure 6 that

1. The DSC endothermic curves of base binders without EC-120 are smooth and flat; there are no endothermic peaks, indicating that their thermal stabilities are good.

2. A strong endothermic peak appears in the interval of 102°C–113°C when EC-120 was added, indicating that the composition has changed in this temperature range. Since the melting point of EC-120 is also about 110°C, it can be concluded that the appearance of endothermic peak is due to the melting of EC-120 after absorbing heat.

3. With the increase of EC-120 contents, the endothermic peak is getting higher and higher, and the areas of them are gradually increased. Since the endothermic peak is caused by the melting of the EC-120, an increase in EC-120 content tends to result in an increase in the endothermic peak area.

### 5. Conclusions

The following conclusions were obtained through macro-performance tests (DSR tests and BBR tests) and microscopic tests (FTIR and DSC) on base asphalt binders, A-70
and SBS I-D, and their warm-mixed asphalt binders with different contents of EC-120.

(1) The addition of EC-120 will enhance the high-temperature rutting resistance of asphalt binder and decrease its low-temperature performance. The impacts increase with the contents of EC-120. The results of FTIR revealed that this is due to the generation of oxides containing carbonyl functional groups after EC-120 was added into asphalt binder.

(2) Comparing the FTIR spectra of asphalt binders before and after adding EC-120, we can find that there is an obvious new peak presented at 1700 cm$^{-1}$, which is a carbonyl group chemically produced between EC-120 and asphalt binder.

(3) DSC curves of base asphalts and corresponding WMA binders are quite different. A strong endothermic peak appears in the interval of 102°C–113°C in the DSC curves of WMA binders. The endothermic peaks and their areas are gradually increased with the increase of EC-120 contents.

(4) DSC tests showed that EC-120 will endothermically melt at the temperature of 102°C–113°C and then play the role in reducing the viscosity of asphalt binder. The greater the dose of EC-120, the greater the enthalpy and the more obvious the effect of reducing viscosity. This is the mechanism that EC-120 can be used to reduce the mixing temperature of asphalt binder.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The authors appreciate the support of the National Natural Science Foundation of China (50878032).

References

[1] M. C. Rubio, G. Martínez, L. Baena, and F. Moreno, "Warm mix asphalt: an overview," Journal of Cleaner Production, vol. 24, pp. 76–84, 2012.
[2] S. D. Capitão, L. G. Picado-Santos, and F. Martinho, "Pavement engineering materials: review on the use of warm-mix asphalt," Construction and Building Materials, vol. 36, pp. 1016–1024, 2012.
[3] S. Sargand, M. D. Nazzal, A. Al-Rawashdeh, and D. Powers, "Field evaluation of warm-mix asphalt technologies," Journal of Materials in Civil Engineering, vol. 24, no. 11, pp. 1343–1349, 2012.
[4] J. R. M. Oliveira, H. M. R. D. Silva, L. P. F. Abreu, and S. R. M. Fernandes, "Use of a warm mix asphalt additive to reduce the production temperatures and to improve the performance of asphalt rubber mixtures," Journal of Cleaner Production, vol. 41, pp. 15–22, 2013.
[5] B. Kheradmand, R. Muniandy, L. T. Hua, R. B. Yunus, and A. Solouki, "An overview of the emerging warm mix asphalt technology," International Journal of Pavement Engineering, vol. 15, no. 1, pp. 79–94, 2014.
[6] A. Almeida-Costa and A. Benta, "Economic and environmental impact study of warm mix asphalt compared to hot mix asphalt," Journal of Cleaner Production, vol. 112, pp. 2308–2317, 2016.
[7] A. Raghavendra, M. S. Medeiros, M. M. Hassan, L. N. Mohammad, and W. B. King, "Laboratory and construction evaluation of warm-mix asphalt," Journal of Materials in Civil Engineering, vol. 28, no. 7, article 04016023, 2016.
[8] A. M. Rodriguez-Alloza, J. Gallego, and I. Perez, "Study of the effect of four warm mix asphalt additives on bitumen modified with 15% crumb rubber," Construction and Building Materials, vol. 43, pp. 300–308, 2013.
[9] A. Buss, R. C. Williams, and S. Schram, “Evaluation of moisture susceptibility tests for warm mix asphalt,” Construction and Building Materials, vol. 102, pp. 358–366, 2016.
[10] A. Chomicz-Kowalska, W. gardziejczyk, and M. M. Iwański, “Moisture resistance and compactibility of asphalt concrete produced in half-warm mix asphalt technology with foamed bitumen,” *Construction and Building Materials*, vol. 126, pp. 108–118, 2016.

[11] L. G. Cucalon, F. Yin, A. E. Martin, E. Arambula, C. Estakhri, and E. S. Park, “Evaluation of moisture susceptibility minimization strategies for warm-mix asphalt: case study,” *Journal of Materials in Civil Engineering*, vol. 28, no. 2, article 05015002, 2016.

[12] J. H. Podolsky, A. Buss, R. C. Williams, and E. W. Cochran, “The rutting and stripping resistance of warm and hot mix asphalt using bio-additives,” *Construction and Building Materials*, vol. 112, pp. 128–139, 2016.

[13] I. Menapace, E. Masad, A. Bhasin, and D. Little, “Microstructural properties of warm mix asphalt before and after laboratory-simulated long-term ageing,” *Road Materials and Pavement Design*, vol. 16, no. 1, pp. 2–20, 2015.

[14] M. D. Nazzal, L. Abu-Qtaish, S. Kaya, A. Abbas, and D. Powers, “A nano-scale Approach to study the healing phenomenon in warm mix asphalt,” *Journal of Testing and Evaluation*, vol. 45, no. 5, article 20150446, 2017.

[15] M. D. Nazzal, L. Abu-Qtaish, S. Kaya, and D. Powers, “Using atomic force microscopy to evaluate the nanostructure and nanomechanics of warm mix asphalt,” *Journal of Materials in Civil Engineering*, vol. 27, no. 10, article 04015005, 2015.

[16] Z. Hossain, S. Lewis, M. Zaman, A. Buddhala, and E. O’Rear, “Evaluation for warm-mix additive-modified asphalt binders using spectroscopy techniques,” *Journal of Materials in Civil Engineering*, vol. 25, no. 2, pp. 149–159, 2013.

[17] D. M. Abd, H. Al-Khalid, and R. Akhtar, “Nano-scale properties of warm-modified bituminous binders determined with atomic force microscopy,” *Road Materials and Pavement Design*, vol. 18, no. 2, pp. 189–202, 2017.

[18] F40-2004, J., *Technical Specification for Construction of Highway Asphalt Pavements*, China Communications Press, Beijing, China, 2004, in Chinese.

[19] X. Tian, H. Han, Q. Zhang, X. Li, and Y. Li, “Design and performance of anticracking asphalt-treated base,” *Advances in Materials Science and Engineering*, vol. 2017, Article ID 2394945, 9 pages, 2017.

[20] X. Tian, Z. Ren, Y. Zhen, C. Yantian, Z. Shaohua, and X. Yichao, “Simulation of bending fracture process of asphalt mixture semicircular specimen with extended finite element method,” *Advances in Materials Science and Engineering*, vol. 2018, Article ID 4081264, 8 pages, 2018.

[21] E. T. Harrigan, R. B. Leahy, and J. S. Youtcheff, The SUPERPAVE Mix Design System Manual of Specifications, Test Methods, and Practices, National Research Council, Washington, DC, USA, 1994.

[22] A. C. S. Talari, M. A. G. Martinez, Z. Movasaghi, S. Rehman, and I. U. Rehman, “Advances in Fourier transform infrared (FTIR) spectroscopy of biological tissues,” *Applied Spectroscopy Reviews*, vol. 52, no. 5, pp. 456–506, 2017.

[23] C. Huaxin, H. Mengshuang, L. Yuanyuan, and Y. He, “DSC analysis on asphalt and asphalt fractions,” *Journal of Chongqing Jiaotong University*, vol. 32, no. 2, pp. 207–210, 2013.

[24] X. Tian, Z. Ren, Y. Zhen, C. Yantian, X. Yichao, and Z. Qisen, “Multiscale study on the effect of nano-organic montmorillonite on the performance of rubber asphalt,” *Journal of Nanomaterials*, vol. 2018, Article ID 9638603, 10 pages, 2018.
