Study on Compatibility Evaluation Method of EC120 Warm Mix Asphalt Binder

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ABSTRACT

The comparability between two modifiers (SBS and EC120) and 70#A basic asphalt was studied. The research was carried out by several approaches: solubility parameter calculation, difference of segregation softening point test, differential scanning calorimetry and atomic force microscope scanning. The results showed that the solubility parameter can not reflect the influence of molecular weight on polymer compatibility. Moreover, due to multi-phase structures with high molecular weight, for both the asphalt and some modifiers, the two blended structures are too complex to apply Hildebrand formula. The addition of EC120 into basic asphalt does not only make glass-transition temperature increase , but also changes the shape of endothermic peak curve significantly, which indicates that EC120 has good compatibility with basic asphalt. The compatibility between modifier and basic asphalt decreases with the addition of SBS and EC120.

KEYWORDS: Road engineering, Warm mix asphalt, Compatibility, Solubility parameter, Atomic force microscope.

INTRODUCTION

In numerous ways, for the implementation of warm mix asphalt technology, EC120 has become one of the main varieties of warm mix modified asphalt for its function of enhancing and improving the pavement performance of asphalt mixture, as well as its low price. However, because of the differences between molecular weights, densities, solubility parameters and other physical and chemical properties among different warm agents with asphalts, the compatibility between them is affected by various factors which make the warm mixing effect and storage stability be affected finally (Wu et al., 2010; Wu and Zeng, 2012).

There are various methods for researching compatibility of modified asphalt. Some of the most common methods, such as: glass transition method, micro-analysis method, FTIR and thermo-dynamic method, are suitable for different situations for the different physical properties of modifiers and basic asphalts. Giovanni et al. (2006) and Fu et al. (2007) researched the influence of species, components and grafting types of SBS modifier on the compatibility with basic asphalts and analyzed the influence of different SBS types on the usability and storage stability of basic asphalts.

Sengoz et al. (2008), Sengoz et al. (2009), Khadiyar and Kavussi (2013) and Zhu et al. (2014) researched the compatibilities between modifiers (SBR, NR, CR

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and EVA) and basic asphalts by using microscopic observation method, image analysis method, particle size analysis method and performance test method, among others. The results showed that the microscopic observation method can yield a better miscibility, which means that the microscopic observation method is the best method for the research of compatibility between modifier and basic asphalt. Research results by Golubev et al. (2003) and Yu et al. (2013) testified the rationality of the microstructure of asphalt binder and its compatibility by atomic force microscopy (AFM) and proposed an appropriate method for sample preparation. The current and widely used method for the evaluation of compatibility between modifiers and basic asphalts is the "Polymer Modified Asphalt Segregation Test (T0661-2011)" documented in *Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering*, since it takes the difference of segregation softening points as the assessment index and is thereby characterized by concisenecss and accessibility. However, it is nothing but a relative characterization method.

For the qualitative evaluation of the compatibility between the warm-mixed modifier EC120 and basic asphalt, this paper studied the theoretical compatibility between the two kinds of modifiers (SBS & EC120) and basic asphalt (70#A) by analysis of solubility parameter δ, compatibility coefficient $\triangle$ and difference of segregation softening points. On this basis, the glass transitions and structural forms of different asphalt binders are studied and measured by differential scanning calorimetry (DSC for short) and AFM, respectively. Compatibility between modifiers and asphalts was analyzed and compatibility between EC120 modifier and basic asphalt was finally obtained.

MATERIALS, METHODS, RESULTS AND DISCUSSION

Raw Materials and Test Methods

i) Raw Materials

Raw materials in this study are as follows: (1) pavement petroleum asphalt level 70#A (basic asphalt) of China Offshore Bitumen Co., Taizhou; (2) Polymer-modified asphalt SBS I-D prepared on the basis of basic asphalt, the main technical parameters of which are shown in Table 1; (3) The admixture of asphalt and EC120 warm mix additive, produced by Sasol Wax Company, which can reduce the mixing and molding temperature of bituminous mixture to 20˚C~30˚C with a percentage of 3%. The main technology parameters of EC120 are shown in Table 2, whereas the technical parameters of warm mix asphalt with 3% EC120 are shown in Table 1. It is shown in Table 1 that basic asphalt and SBS-modified asphalt conform with the regulations in *Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering* (JTG F40-2004).

Table 1. Main technical indices of asphalt binders

Index	Unit	70#A Basic Asphalt	SBS Modified Asphalt	EC120 Warm Mix Asphalt
Penetration (25˚C, 5s, 100g)	0.1mm	76	58	50
Penetration Index *PI*	--	-0.8	0.33	0.30
Softening Point $T_{R\&B}$ (not less than)	˚C	46.4	68.0	77.0
Ductility (10˚C, not less than)	cm	46	63	28
Ductility (15˚C, not less than)	cm	＞100	81	＞100
Density（15˚C）	g/cm^3	1.010	1.029	1.013

Table 2. Basic technical indices of EC 120 warm mix additive

Melting Point (˚C)	Flashing Point (˚C)	Viscosity (135˚C, Pa・s)	Penetration (25˚C, 0.1mm)	Penetration (65˚C, 0.1mm)	Density (25˚C, g/cm^3)
98~100	269	0.01~0.012	≤1	8	0.79

ii) Method of Sample Preparation

In order to ensure the acquisition of information that can directly reflect nano-scale surface properties of asphalt binder, samples in theory should be fine dispersed and uniformly distributed. For the credibility of the test results, one-time blending method was used in the preparation of modified asphalt samples and a colloid mill (2000 mesh) imported from Germany was used for grinding the modified asphalt to make modifiers and asphalts fully mixed. Rotational velocity was 4500 rpm and grinding time was 4h. The detailed preparation process is shown in Fig. 1.

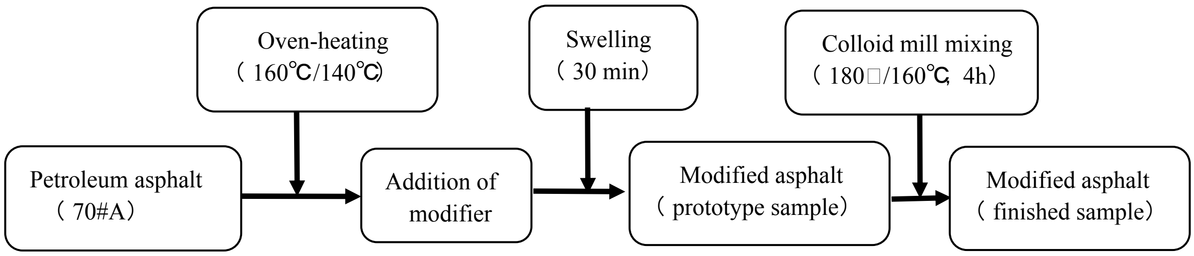


Figure (1): Preparation process flow chart for modified asphalt

iii)Test Methods

(1) Segregation Softening Point Test

Segregation softening points of different asphalt binders were tested according to *Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering* (JTG E20-2011).

(2) DSC Test

Thermal properties of different asphalt binders were analyzed by simultaneous thermal analyzer type STA 449F3 produced by NETZSCH Co. The test process is as follows: Put about 10 mg DSC into a special aluminum pan for DSC and raise the temperature from the balanced initial temperature of – 40ºC to 100ºC at a rate of 2ºC/min, then lower the temperature back to -40ºC and keep this temperature constant for 2h to eliminate thermal history. Then, test for next sample can be conducted.

(3) AFM Test

All of the AFM tests were conducted through the Digital Instruments-Veeco Metrology Group AFM with 180×180 image resolution and 15μm×15μm scanned area working at tapping mode. In the test, feature points on the sample surface were found by probe and the images were scanned and then further processed by system analysis software. At least, 8-10 feature points were scanned and processed for each of the samples.

Research on the Compatibility of Asphalt Binder Based on Solubility Parameters and Differences of Segregation Softening Points

The compatibility between modifier and solvent can be forecasted by solubility parameter based on Hildebrand theory. The less the solubility parameter between modifier and basic asphalt and the compatibility coefficient △, the better the compatibility between modifier and asphalt; the more the dose of modifier and the compatibility coefficient △, the worse the compatibility between modifier and asphalt. There is a direct relationship between the solubility parameter and the proportion of each component. Basic composition of materials and the corresponding solubility parameters δ are shown in Table 3, where the units are transformed into the statutory measurement ones, using the formula $1J^{1/2}/cm^{3/2} = 4.1868 \times 10^6 J/m^3 = 2.046\ MPa^{1/2}$.

Table 3. Chemical composition and soluability parameter of each material

Type of Material	Chemical Composition	δ（$J^{1/2}/cm^{3/2}$
70#A Basic Asphalt	Asphaltene	10.93
	Colloid	10.93
	Aromatics	9.15
	Saturates	7.45
SBS (Styrene-Butadiene-Styrene Block Copolymer)	Polystyrene (PS)	9.10
	Polybutadiene (PB)	8.40
EC120（Polyolefin Stem）	Long Chain Aliphatic (Major Component)	14.79

It is shown in Table 3 that: (1) the solubility parameter of fragment PS of SBS is similar to that of aromatics and colloid of basic asphalt and fragment PS of SBS is similar to that of aromatics and saturates of basic asphalt. In comparison with fragment PB, the relative molecular mass and polarity of fragment PS are closer to those of basic asphalt and the aromatics and saturates are in relatively high levels in asphalt, so that the compatibility of fragment PS is better than that of fragment PB in the SBS-basic asphalt blend system. (2) The main chemical composition of EC120 is polyolefin stem whose nature is aliphatic hydrocarbon of chemical structure $-CH_3$ and $-CH_2$ with the longer carbon chain. Its solubility parameter is more close to the solubility parameter of the asphaltene and colloid of basic asphalt. However, the difference between them is more than 3.0 (14.79-10.93=3.86), so that it can be concluded that EC120 warm mix additives and basic asphalt are incompatible systems according to the solubility parameter theory.

For further evaluation of compatibility between modifiers and basic asphalt, the differences of separation softening points of testing regulations T0661-2011 added as the evaluation indices and the indices of basic asphalts modified by different modifiers were measured, see Table 4.

From Table 4, it is obvious that the difference of solubility parameter δ between EC120 and basic asphalt is relatively large (5.32), while the corresponding value between SBS and basic asphalt is relatively small (0.86). According to Hildebrand theory, EC120 is incompatible with basic asphalt, but SBS can be well compatible with it. In sense of differences of separation softening points, the value of EC120 warm mix asphalt is 6.5℃ less than that of SBS- modified asphalt, which shows that the variability of separation softening point of warm mix asphalt binder is small and warm mix asphalt binder has a better compatibility than SBS. For the other parameter, the compatibility coefficient △ of EC120 warm mix asphalt is much larger than that of SBS-modified asphalt and is completely incompatible with basic asphalt from the perspective of numerical values.

From the analysis above, it is not objective to simply evaluate compatibility between the modifier and the basic asphalt by solubility parameter δ, compatibility coefficient △ and differences of separation softening points. The specific reasons are as follows: (1) Hildebrand theory considers the structure unit of modifier only and fails to give consideration to the difference of molecular weights between modifier and basic asphalt. (2) Hildebrand theory only applies to nonpolar molecules, for this theory only considers dispersion forces between molecules and fails to give consideration to the dipole forces and hydrogen bonds. (3) The assessment conclusion of the compatibilities of the three parameters is inconsistent.

Table 4. Test and calculation results for compatibility of different modifiers and basic asphalt

Type of Material	**70#A Basic Asphalt**		**SBS Modified Asphalt**	**EC120 Warm Mix Asphalt**
Constituents	Asphaltene (%)	5.21	5%SBS+ 95%70#A	3%EC120 +97%70#A
	Colloid (%)	26.39		
	Aromatics (%)	48.84		
	Saturates (%)	19.56		
Solubility Parameter δ of Basic Asphalt or Modifier ($J^{1/2}/cm^{3/2}$)	9.47		8.61	14.79
Difference to Solubility Parameter δ of Basic Asphalt ($J^{1/2}/cm^{3/2}$)	0		0.86	5.32
Softening Point (℃)	46.4		68.0	77.0
Difference of Separation Softening Points (˚C)	1.3		10.3	3.8
Compatibility Parameter $\triangle$ to Basic Asphalt (%)	--		10.53	79.26

In conclusion, it is not possible to determine the compatibility between the modifier and the basic asphalt effectively through the solubility parameter or segregation softening point only. Other methods must be combined for comprehensive judgement.

Research on the Compatibility of Asphalt Binder Based on DSC

Results of DSC tests of 3 kinds of asphalt binders are shown in Fig. 2 and Table 5.

Table 5. DSC characteristic data of various asphalt binders

Measuring Parameters	**70#A**	**SBS**	**70#A+EC120**
Inital Temperatures of the Change of Endothermic Peak (ºC)	47.2	34.7	33.6
Peak Temperature of Endothermic Peak (ºC)	58.9	43.2	52.9
Area of Endothermic Peak (mJ)	19.743	35.670	61.675
Caloric Value of Endothermic Peak (mJ/mg)	1.241	2.153	5.966
Glass-transition Temperature T_g (ºC)	-8.7	-10.7	-6.9

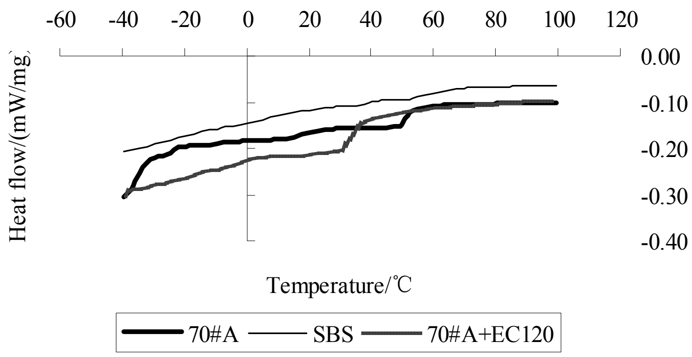


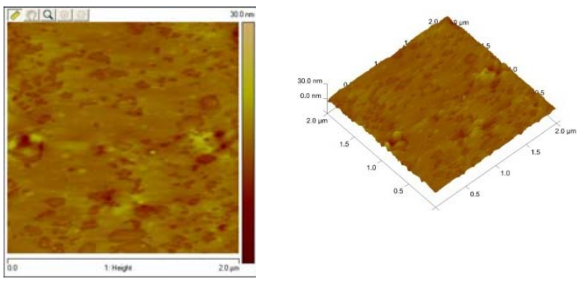
Figure (2): DSC curve of various asphalt binders

Results of the DSC test indicated that: (1) Glass-transition temperature T_g is an effective means of judging the compatibility between two kinds of polymers after alloying. In the temperature range -40ºC～100ºC, basic asphalt shows glass-transition at a relatively low temperature (-30ºC～ -10ºC) and an endothermic peak over a very wide temperature range above the glass-transition temperature T_g which is because of the fusion of wax components and naphthenic aromatics crystallization at high temperatures. (2) The addition of SBS reduces T_g of basic asphalt and the DSC curve no longer shows a steep shape, which means that there is good compatibility between the modifier SBS and the basic asphalt, as the melting temperature of asphalt binder is raised. During the heating process, asphalt will be bound in the cross-linked network formed of polymers gradually, so its melting temperature increases accordingly. (3) The addition of EC120 will not only raise T_g of the binder, but the hot melt peak after T_g also occurs earlier, which means that EC120 has a good compatibly with the matrix asphalt and the thermoplastic behavior of asphalt has changed fundamentally after the fusion. EC120 raised T_g of asphalt and reduced its viscosity at the same time.

Research on the Compatibility of Asphalt Binders Based on AFM

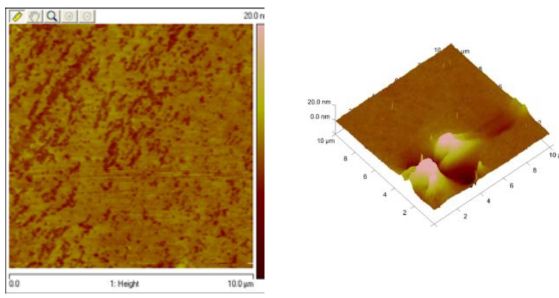
i) Test Results

There are 4 kinds of samples for the test; namely: 70#A basic asphalt, SBS-modified asphalt level I-D, 70#A+EC120 warm mix asphalt and SBS+EC120 warm mix asphalt. AFM test results of the binders are shown as follows:



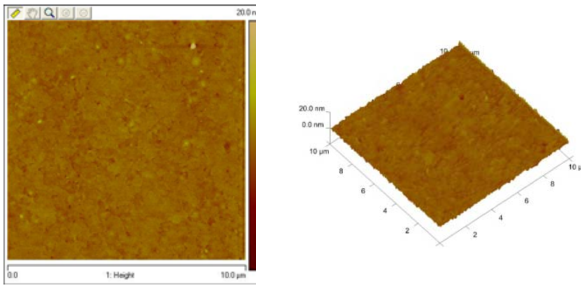
(a) Micrograph of 5# Point (b) Stereogram of 5# Point

Figure (3): AFM images of 70#A basic asphalt



(a) Micrograph of 3# Point (b) Stereogram of 9# Point

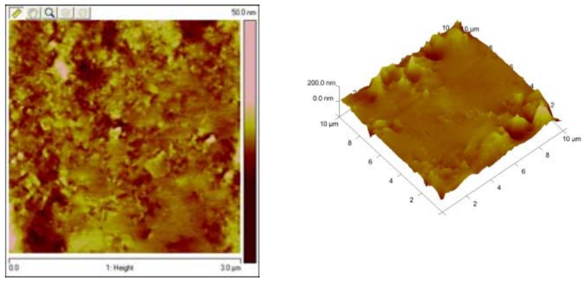
Figure (4): AFM images of SBS-modified asphalt



(a) Micrograph of 6# Point

(b) Stereogram of 6# Point

Figure (5): AFM images of 70#A + EC120 warm mix asphalt



(a) Micrograph of 7# Point

(b) Stereogram of 4# Point

Figure (6): AFM images of SBS+ EC120 warm mix asphalt

The test results show that:

(1) The topographies and stereograms of AFM results can clearly reflect the surface flatness (roughness) of the samples. Surface topography of 70#A basic asphalt is the most smooth one, because there is no additive in it, even though there are some small pit slots on its surface. The distribution is relatively homogenous and the vertical height on axis Z is 5.2 nm on average.

(2) SBS can form an uniform and stable stereoscopic network system with basic asphalt in order to blend uniformly under the high speed shearing action from the colloid mill (as shown in Fig. 4(a)). Even though there are some relatively large polymer particles distributed (the highlighted area shown in Fig. 4(b)), but the overall degree of dispersion of SBS in basic asphalt is in a high level and the vertical height on axis Z is 7.5 nm on average and less than 20 nm for the largest value.

(3) Compared with SBS, the apparent morphology of 70#A+EC120 warm mix asphalt binder is relatively smooth (as shown in Fig. 5), because EC120 is dissolved in the asphalt at a definite temperature (120℃) and the vertical height on axis Z is relatively small (6.2 nm on average).

However, the apparent morphology of SBS+EC120 warm mix asphalt binder is relatively rough with uneven pit slots and uneven arrangement (as shown in Fig. 6). The vertical height on axis Z is 48.9 nm on average and 167 nm for the largest value, which means that the addition of modifier SBS with warm mix additive EC120 into basic asphalt will obviously increase the particle size and dispersion degree of blending particles. As a result, viscosity of SBS+EC120 warm mix asphalt binder is larger than that of 70#A+EC120 warm mix asphalt binder and its compatibility is much worse than that of 70#A+EC120 warm mix asphalt binder.

ii) Compatibility Evaluation

AFM test can evaluate the compatibility between modifier and basic asphalt from a microcosmic view, coming to the following conclusions: The modifiers SBS and EC120 both have good compatibility with the basic asphalt, the addition of the composite modifier significantly reduces the compatibility between the additive and the basic asphalt and it is suggested that it's better to reduce the usage of the composite blend of modifier SBS and warm agent EC120 as far as possible in practical applications.

CONCLUSIONS

i) Solubility parameter δ can't reflect the influence of the molecular weight on the compatibility of polymer. As the asphalt and some kinds of modifiers are multiple structures of high molecular weights and the structures are even more complicated after blending, the compatibility between modifier and basic asphalt can't be evaluated using Hildebrand theoretical formula by recognizing the individual as a whole.

ii) Relatively obvious swelling reaction of basic asphalt happened because of the addition of polystyrene into SBS-modified asphalt, which changed T_g of the asphalt binder and the shape of the asphalt endothermic peak curve. It is certain that SBS and basic asphalt are a biphase compatible system with good compatibility combined with the differences of separation softening points and test results of AFM.

iii) The addition of EC120 will not only raise T_g of the basic asphalt, but will also change the shape of the basic asphalt endothermic peak curve. It is certain that EC120 and basic asphalt are a biphase compatible system with good compatibility combined with the differences of separation softening points and test results of DSC and AFM.

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