

Influence of modification process parameters on the properties of crumb rubber/EVA modified asphalt

Changqing Fang,¹ Xiaoting Qiao,¹ Ruien Yu,¹ Xin Yu,¹ Jianjun Liu,² Jiang Yu,¹ Ronghou Xia¹

¹Faculty of Printing Packaging Engineering and Digital Media Technology, Xi'an University of Technology, Xi'an, 710048, Shaanxi, People's Republic of China

²The 43rd Institute of the Fourth Academy of CASC, Xi'an, Shaanxi, 710025, People's Republic of China Correspondence to: C. Fang (E-mail: fcqxaut@163.com)

ABSTRACT: Crumb rubber (CR) and ethylene vinyl acetate copolymer (EVA) were adopted as asphalt modifiers. Routine tests, softening point, penetration, and ductility were used to evaluate the basic properties of crumb rubber and ethylene vinyl acetate copolymers (CR/EVA) modified asphalt. The segregation experiment measured the storage stability. Modern test methods such as fluorescence microscopic photography technology was used to study stability of polymer modified asphalt. Infrared spectrum experiment was used to analyze the composition differences of the upper part and lower part of CR/EVA modified asphalt. Matlab software was employed to fit out the formulae of ductility, penetration, and softening point difference of modified asphalt and shearing temperature, shearing time and shearing rate separately. Compared with base asphalt, the properties of CR/EVA modified asphalt have been greatly improved. The formulae which were fitted out by Matlab software showed that the shearing time was the foremost factor affecting the properties of CR/EVA modified asphalt, followed by shearing temperature, and the last was shearing rate. The conclusions which were fitted by orthogonal experiment were basically consistent with the results of formulae which were fitted out by Matlab software. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43598.

KEYWORDS: applications; composites; copolymers; properties and characterization; rubber

Received 14 August 2015; accepted 2 March 2016 DOI: 10.1002/app.43598

INTRODUCTION

Asphalt, with a kind of colloid structure, is a product of crude oil distillation. The material of asphalt is composed of some extremely complex polymer hydrocarbons and nonmetal (oxygen, sulfur, and nitrogen) derivatives of the mixture.^{1,2} Petroleum asphalt has strong adhesion, good viscoelasticity, and many excellent properties, such as paving of cement pavement with driving comfort, low noise, and the advantages of small vehicle wear and tear, so petroleum asphalt is widely used. Now the increasing traffic volume, vehicles, bigness overload transportation is more serious, difference in temperature is very large in many parts, bituminous pavement cannot meet the heavy load of modern traffic.³ Therefore, modified asphalt has become a hot topic in recent decades.^{4–6} There are mainly three kinds of polymers in modifying asphalt, rubber, resins, and plastics.⁷⁻⁹ Crumb rubber (CR) and ethylene vinyl acetate (EVA) are used as modifiers for modified asphalt in this research. With the development of our living conditions, the scale of cars increases annually. Waste rubber tires, as the "black pollution," have already become a public problem throughout the whole world. Crumb rubber has been used as an environmental material and it can produce pavement with good

mechanical behavior, reduce the noise caused by traffic as well as road maintenance costs.^{10–12} CR and EVA are employed as modifiers, it can save resources, cost and reduce "black pollution".¹³ The viscosity of roads in summer, and cracking and slipping in winter can be prevented or reduced. As a result, using CR and EVA in modified asphalt has already attracted more attention in many countries.¹⁴

Many scholars have conducted studies on modified asphalt. Huang¹⁵ found that crumb rubber powder modified asphalt can improve the fatigue resistance to a great extent. Bahia¹⁶ found that the properties of modified asphalt are decided by many elements, such as particle size of the crumb rubber powder and chemical/ physical properties of base asphalt, as well as its source, and modified asphalt processing technology and so on. Liu¹⁷ used variance analyze to analyze the various factors affecting the property of crumb rubber modified asphalt. He showed that among the three factors of crumb rubber type, particle size, and content, the content is foremost factor affecting the properties of CRM asphalt, followed by crumb rubber type, and particle size comes last. Navarro¹⁸ studied the storage stability of rubber modified asphalt.

© 2016 Wiley Periodicals, Inc.



Table I. Properties of Base Asphalt

Properties	Penetration	Softening	Ductility
	(25 °C) (0.1 mm)	point (°C)	(5 °C) (cm)
Base asphalt	68	48.7	1.5

stored stability of the modified asphalt system and led to the distribution of the rubber particles in system changes. Zhang^{19,20} studied aging as an influence of SBS/sulfur modified asphalt rheological properties. Results showed that the addition of sulfur led to the formation of a system network structure, so that it could dramatically improve the thermal stability of SBS modified asphalt. Liang²¹ investigated the rheological properties and storage stability of CR/SBS modified asphalt and found that storage stability was detected by microscopy and mechanical properties. Ye²² established a model for the quantitative relationship between temperature and microstructure of Styrene-Butadiene-Styrene modified asphalt and the model would be useful to study the temperature sensitivity of different kinds of modified asphalt and make quantitative comparison between them. Fang²³ studied preparation process to affect stability in waste polyethylenemodified bitumen and he found that the thermal stability of the modified bitumen surpassed that of the base bitumen, but was generally independent of the preparation parameters.

There are many published articles about the polymers in modifying asphalt. However, most of the asphalt modifications are basically based on only one kind of modifier in many researches. Moreover, a qualitative analysis has not been made on the factors affecting the properties of modified asphalt. The properties of high and low temperature of asphalt cannot be improved by one modifier at the same time. So this article will supply a qualitative analysis about the factor which will affect the performances of the modified asphalt and two modifiers are used. As one kind of analysis software, Matlab could get formulae according to the lab data. In this article, two kinds of modifiers were used for modifying asphalt: CR is a kind of rubber and EVA is a kind of resin; use these two kinds of modifiers, the low and high temperature properties of asphalt could be improved simultaneously. The main objectives of this study are described below: the properties of CR/ EVA modified asphalt are investigated; storage ability of CR/EVA modified asphalt is studied; the linear relationship among the properties of modified asphalt and the modification process are studied and Matlab software is used to establish equations concerning shearing time, shearing temperature and shearing rate as independent variables while softening point, penetration, ductility, and softening point difference are dependent variables, respectively. Orthogonal experiment was used to further discuss the relationship between process conditions and properties of CR/ EVA modified asphalt.

EXPERIMENTAL

Materials

The base asphalt used in this study was SK-70. The conventional characterization results of base asphalt are displayed in Table I. The average molecular weight of EVA was about 2000 g/mol.

The Preparation of CR/EVA Modified Asphalt Samples

The concentration of CR was 5% by weight and EVA was 2%. Base asphalt was melted at about 100 $^{\circ}$ C; after that CR and EVA were added and then base asphalt was modified at a particular shearing temperature, shearing time and shearing rate. Three different kinds of shearing temperature, shearing time, and shearing rate were analyzed in this article. The modification process of each sample is shown in Table II.

Test Methods

Penetration at 25 °C, softening point and ductility at 5 °C were measured as conventional tests. Penetration, ductility, and softening point of asphalt were tested by penetration, ductility, and softening point instruments, respectively.

A segregation test is a conventional method which is used to evaluate the storage stability of polymer modified asphalt. Asphalt is heated until it flowed adequately and erected into an upright tube; the quantity is about 50 g. Then, the sample with tube is placed in an oven vertically at a temperature setting of 163 $^{\circ}$ C for 48 h. Next, the tube is put into a refrigerator for cooling not less than 4 h. When it fully cooled, the tube is divided into three equal sections. Finally, samples from the

Table II. The Modification Process of Each Sample

Sample number	Temperature (°C)	Time (h)	Rate (r/min)
Sample 1	160	1.5	1250
Sample 2	160	1.5	2500
Sample 3	160	1.5	3750
Sample 4	140	1.5	1250
Sample 5	140	1.5	2500
Sample 6	140	1.5	3750
Sample 7	120	1.5	1250
Sample 8	120	1.5	2500
Sample 9	120	1.5	3750
Sample 10	160	1	1250
Sample 11	160	1	2500
Sample 12	160	1	3750
Sample 13	140	1	1250
Sample 14	140	1	2500
Sample 15	140	1	3750
Sample 16	120	1	1250
Sample 17	120	1	2500
Sample 18	120	1	3750
Sample 19	160	2	1250
Sample 20	160	2	2500
Sample 21	160	2	3750
Sample 22	140	2	1250
Sample 23	140	2	2500
Sample 24	140	2	3750
Sample 25	120	2	1250
Sample 26	120	2	2500
Sample 27	120	2	3750



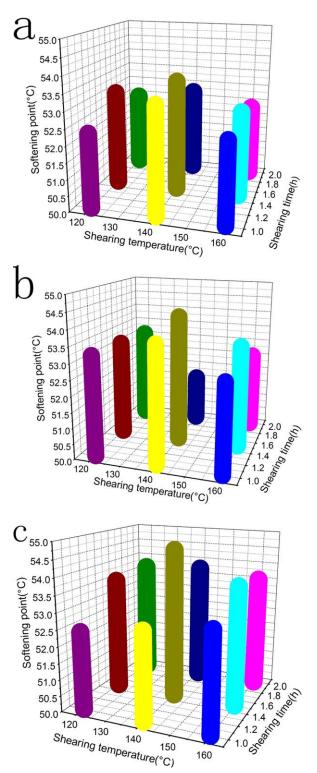


Figure 1. Relationship between softening point and shearing time, shearing temperature (a) 1250 r/min; (b) 2500 r/min; and (c) 3750 r/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

upper and lower sections of the tube are tested in softening point instrument and the difference between the upper and lower sections was calculated. Microscopic photography is one of the effective methods to study stability of polymer modified asphalt. The state of polymer within base asphalt is observed by fluorescence microscopy. CR/EVA modified asphalt was heated to melt and then a small amount of molten samples were loaded between two glass slides. After being cooled at room temperature for 24 h, it was observed in the fluorescence microscope.

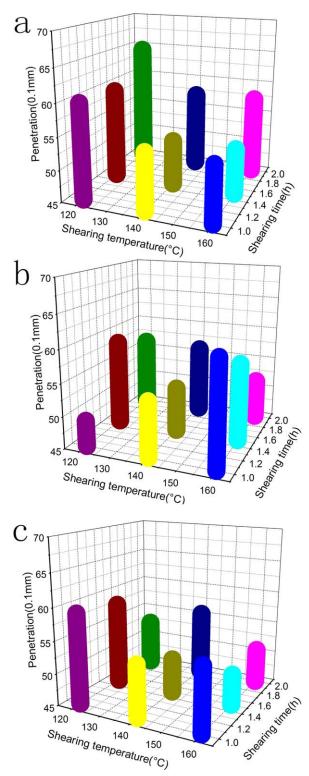
Infrared spectrum experiment can analyze the composition differences of the base asphalt and modified asphalt. About 100 mg dry potassium bromide is grinded into powder in agate mortar uniformly. The powder is transferred to special tablet machine for dying. Then the base asphalt and modified asphalt is melt on the stove and smeared evenly onto the KBr chip. When the tube is cooled down to room temperature and then measured in the light path system.

RESULTS AND DISCUSSION

Influence of Shearing Temperature on the Properties of CR/EVA Modified Asphalt

Shearing temperature was an important parameter in the preparation of modified asphalt. It had a great effect on the properties of CR/EVA modified asphalt. Softening point reflects the temperature sensitivity of asphalt. When softening point is high, both temperature stability and thermal stability are good. When the shearing rate was 1250, 2500, and 3750 r/min, threedimensional relationships of shearing time, shearing temperature, and softening point are shown in Figure 1(a-c). As can be observed in Figure 1, softening point of asphalt which was modified by CR and EVA increased from the previous unmodified 48.7-54.6 °C, it increased in the range of 6 °C. That is to say that the high temperature property of modified asphalt was well improved. With the increase of temperature, softening point started decreasing after increasing and reached a maximum at 140 °C. The softening point of modified asphalt was determined by the size of the asphalt molecular weight. When the molecular weight was larger, the movement required to overcome the frictional resistance was greater, that the softening point of asphalt will increase.

With shearing temperatures of 160, 140, and 120 °C, fluorescent microscopy images of modified asphalt are shown in Figure 5. As can be seen in Figure 5, modifiers dispersed in the base asphalt and white polymer with spherical shape of modified asphalt was distributed in base asphalt. Meanwhile, there were a number of small particles dispersed around the larger particles. When the stirring temperature was low, the motion degree of the molecular chain was relatively small; its viscosity was bigger which was not conducive to mix CR, EVA and asphalt homogeneously. In this way, asphalt molecules became integrated with EVA and the network structure of CR, which made the molecular weight of modified asphalt comparatively small. Therefore, the softening point was relatively low. When the temperature was high, the molecular chain of the asphalt system with CR/ EVA blended well and made the molecular weight of modified asphalt increase, so the softening point improved. When the temperature was high once again, although the molecular chain of asphalt system and CR/EVA were evenly distributed, due to the breaking strength of CR, the high elasticity of the resin



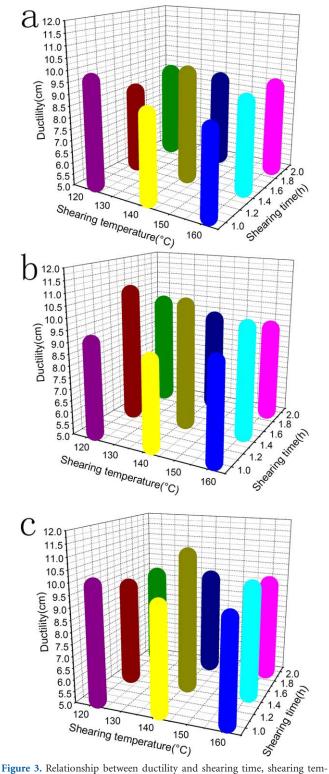


Figure 2. Relationship between penetration and shearing time, shearing temperature (a) 1250 r/min; (b) 2500 r/min; and (c) 3750 r/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

perature (a) 1250 r/min; (b) 2500 r/min; and (c) 3750 r/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

would reduce and the softening point would decrease. Asphalt modification would lose its significance. Selected by the above analyze, the shearing temperature at 140 $^\circ \rm C$ was more appropriate.

Penetration is a representation of the consistency of asphalt. When the shearing rate was 1250, 2500, and 3750 r/min, threedimensional relationships of shearing time, shearing temperature,

Applied Polymer

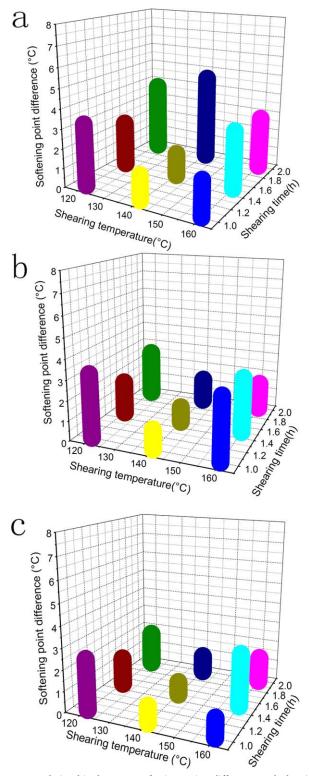


Figure 4. Relationship between softening point difference and shearing time, shearing temperature (a) 1250 r/min; (b) 2500 r/min; and (c) 3750 r/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and penetration are shown in Figure 2(a-c). As can be observed in Figure 2, penetration of base asphalt was 6.8 mm. After being modified by CR and EVA, the penetration maximum was

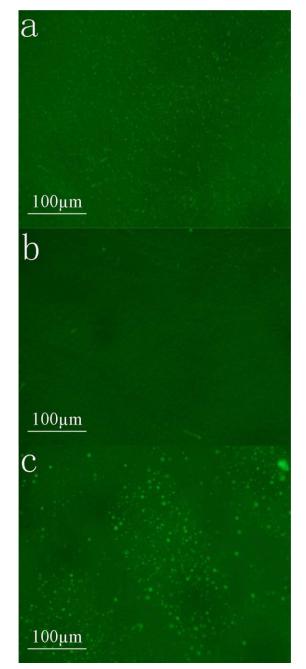


Figure 5. Fluorescent microscopy images of modified asphalt (a) 160 °C; (b) 140 °C; (c) 120 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

5.95 mm, while the minimum was 4.85 mm. Thus penetration was greatly improved. Ductility could reflect the low temperature property of asphalt. It is a deformational ability at a certain temperature before the tension and it is one of the most important indicators of road asphalt. The higher ductility is, the larger deformation capacity of low pitch is. When the shearing rate was 1250, 2500, and 3750 r/min, three-dimensional relationships of shearing time, shearing temperature and ductility are shown in Figure 3(a–c). As can be seen from Figure 3, ductility of base asphalt was 1.5 cm. However, minimum ductility of CR/EVA modified asphalt was

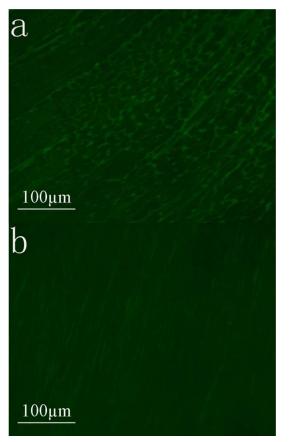


Figure 6. Fluorescence microscopy figures of modified asphalt (a) upper part; (b) lower part. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

8.1 cm. Compared with base asphalt, the ductility increased more than four times. It showed that modified asphalt in the low temperature crack resistance had greatly improved. Asphalt is a kind of polymer mixture with organic compounds. The viscosity of asphalt is very large and it would increase as the temperature gradually increased. From Figures 2 and 3, and 5(c), it was not conducive to stir because of the effect of viscosity when the temperature was too low. Therefore, CR and EVA were not fully dissolved in the asphalt. Part of CR in the asphalt formed small masses on the macro property, and the surface of the asphalt was rough. When the temperature increased, the elastic modulus of EVA quickly decreased and the surface particles of EVA were rough at the same time. Because of the increase in temperature, stress concentration might be formed. Although it could reduce the viscosity of asphalt, the asphalt oxidized exceedingly under high temperature. Furthermore, it reduced the properties of asphalt and made asphalt ductility decrease. However, in Figure 5(a), although CR, EVA dispersal in the asphalt was better when the temperature is too high, it is likely to make the asphalt rapidly age. It could not meet the modification effect. So the mixing temperature selected at about 140 °C was more appropriate.

The storage stability of polymer modified asphalt means polymer did not degrade or segregate in the process of production, storage, and usage. The storage stability of polymer modified asphalt was mainly determined by the compatibility of polymer

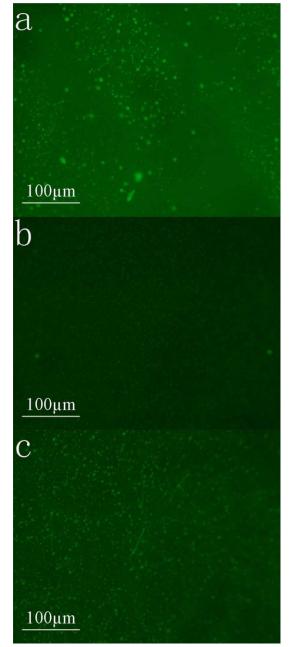


Figure 7. Fluorescent microscopy images of modified asphalt (a) 1 h; (b) 1.5 h; and (c) 2 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and asphalt generally. The better the compatibility was, the greater the stability of the polymer modified asphalt was. Technical specification for construction of highway asphalt pavement in our country stipulated that the softening point difference between the upper and lower parts should not be more than $2.5 \, {}^{\circ}\text{C}^{.24}$ The degree of segregation in the process of polymer storage was small and the storage was steady. This subject adopted the conventional segregation test to evaluate the storage stability of modified asphalt. The size between the upper and lower sections could reflect the extent of the storage stability of modified asphalt. Microscopy figures of upper and lower parts



Applied Polymer

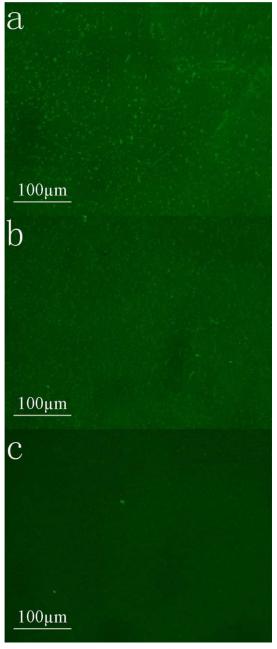


Figure 8. Fluorescent microscopy images of modified asphalt (a) 1250 r/min; (b) 2500 r/min; and (c) 3750 r/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are illustrated in Figure 6. As can be seen from Figure 6, compared with the upper part, the mass of CR and EVA in the lower part was relatively less. It meant that the amount of modifiers in the upper part was higher than lower part, so the softening point of upper part was higher than lower part. This was a reason why the softening point had a gap between the upper and lower parts. When the shearing rate was 1250, 2500, and 3750 r/min, three-dimensional relationships of shearing time, shearing temperature, and softening point difference is shown in Figure 4(a–c). It is illustrated in Figure 4 that the softening point difference of CR/EVA modified asphalt was less than 2.5 °C. It showed that the compatibility of modifiers and

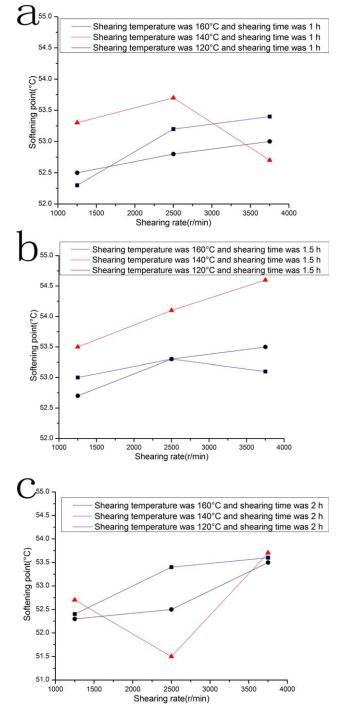


Figure 9. Relationship between softening point and shearing rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

asphalt were improved to a certain extent. So it met the technical specification for construction of highway asphalt pavement in China.

Influence of Shearing Time on the Properties of CR/EVA Modified Asphalt

Shearing time was an important parameter in the preparation of modified asphalt. As can be seen from Figures 1–4, the



softening point and ductility of modified asphalt showed a downward trend after the first rise, and penetration and softening point difference increased after the first drop. In the shearing process, part of CR had desulfurization and degradation, which broke the mesh structure to a certain extent. As can be observed in Figure 7, in a certain time, with the extension of time, EVA and CR particles became smaller and dispersed into the asphalt binder. EVA formed a grid structure in the asphalt. CR/EVA interacted with the asphalt. So the softening point was on the rise, while the softening point difference was on the decline. At the same time, when CR contacted with the asphalt, it would immediately swell, and then the size of rubber particles could get bigger, which would increase the resistance of rubber particle displacement. The viscosity of the system would improve; swelling of CR increased the interface thickness of asphalt and rubber particles; the affinity of asphalt and rubber particles aggrandized simultaneously. Therefore, the ductility of modified asphalt added consequently. While continuing to cut, desulfurization and degradation of CR would happen excessively. Besides, high temperature for a long time made the asphalt age. When shearing time was short, CR/EVA and asphalt could not mix uniformly; however, if the shearing time was too long, aging of the asphalt may occur, so the properties of modified asphalt decreased. Then, the proper shearing time was 1.5 h.

Influence of Shearing Rate on the Properties of CR/EVA Modified Asphalt

Fluorescent microscopy images of modified asphalt which under different rate are shown in Figure 8. The relationship between softening point, ductility, penetration, softening point difference, and shearing rate are shown in Figures 9-12. As can be seen from Figures 9-12, with the increase of shearing rate, softening point, and ductility basically increased, softening point difference and penetration basically decreased. Figure 8 shows that when the shearing time was regulated, the greater the shearing rate was, the more finely polymer modifiers dispersed, the smaller the polymer particle size was and the bigger the specific surface area was. CR/EVA dispersed better in asphalt and the system of modified asphalt was more stable. In this case the particles became gradually smaller and the modifier dispersed more evenly in the asphalt. Then particles of polymer would absorb the more asphalt components to reduce the surface energy which makes the distance between the colloid and asphalt colloid decrease. However, the interaction force increased and the space three-dimensional network structure was more stable. The formation of this structure had a constraint effect on the flow and sliding deformation of asphalt molecules. Therefore, high and low temperature properties of asphalt were improved. However, the shearing rate was too high; it might make CR degrade excessively.²⁵ So it would affect the properties of modified asphalt.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The infrared spectra of base asphalt and modified asphalt were shown in Figure 13. Two obvious absorption peaks were appeared in 2917 and 2857 cm⁻¹. The peak was aroused by asymmetric contraction of C—H bond in 2917 cm⁻¹ and symmetrical contraction of C—H bond in 2857 cm⁻¹. These can

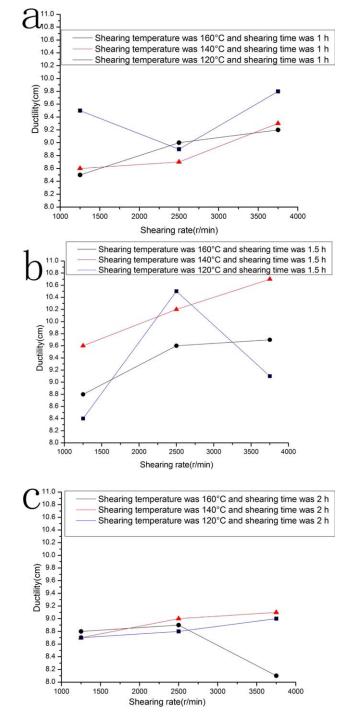


Figure 10. Relationship between ductility and shearing rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

explain that after modifiers added to asphalt, modifiers absorb saturated points of base asphalt and this can cause the movement pitch of the molecular chain segment.

A small absorption peak appeared after the asphalt modified in 1739 cm^{-1} . This is a characteristic peak which was caused by stretching vibration of C=O in EVA modifier and the peaks in 1595 and 1458 cm⁻¹ were caused by C=C and C=O of asphalt.



 $a_{{}^{\scriptscriptstyle{5.7}}_{\scriptscriptstyle{5.4}}}^{{}^{\scriptscriptstyle{6.0}}}$

5.1 -4.8 -

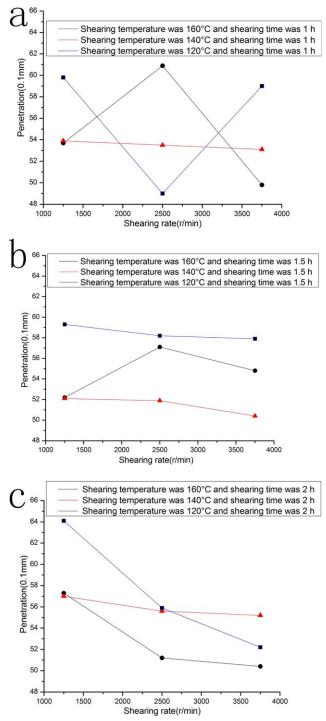
4.2 -

3.6 -3.3 -3.0 -

Applied Polymer

Shearing temperature was 160°C and shearing time was 1 h Shearing temperature was 140°C and shearing time was 1 h

Shearing temperature was 120°C and shearing time was 1 h



Softening point difference(°C) 2.7 2.4 2.1 1.8 1.5 1.2 -0.9 -0.6 0.3 0.0 1500 2000 2500 3000 3500 4000 1000 Shearing rate(r/min) 5.7 -5.4 -Shearing temperature was 160°C and shearing time was 1.5 h Shearing temperature was 140°C and shearing time was 1.5 h 5.1 -Shearing temperature was 120°C and shearing time was 1.5 h 4.8 -4.5 -Softening point difference (°C) 7.2 3.9 7.2 1.1 7.2 1. 1.2 -0.9 -0.3 0.0 -1500 2000 2500 3000 3500 4000 1000 Shearing rate(r/min) 6.0 5.7 5.4 Shearing temperature was 160°C and shearing time was 2 h Shearing temperature was 140°C and shearing time was 2 h Shearing temperature was 120°C and shearing time was 2 h 0.9 0.0-1500 2000 2500 3000 3500 4000

Figure 11. Relationship between penetration and shearing rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Stretching vibration of unsaturated bond is an important feature of the aromatics in modified asphalt among $2400-1500 \text{ cm}^{-1}$.

The infrared spectra of upper and lower parts of modified asphalt are shown in Figure 14. It can be seen from above: positions of the peaks of upper and lower parts were the same because of the same modified asphalt compositions. A small absorption peak appeared in 1163 cm⁻¹; and this is a characterFigure 12. Relationship between softening point difference and shearing rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Shearing rate(r/min)

istic peak which was caused by the inner surface of the bending vibration of =C-H in butadiene rubber component of CR. It can be found that the peak of upper part was stronger than peak of lower part in 1163 cm⁻¹. Under the condition of high temperature during the process of asphalt storage, the upper part of the CR content was higher, because the density of CR was relatively light under the action of heat and CR slowly gathered to the surface of asphalt.

WWW.MATERIALSVIEWS.COM

1000

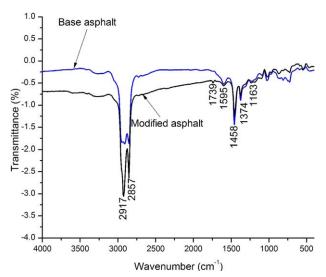


Figure 13. Infrared spectra of base asphalt and modified asphalt. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

Linear Relationship Analysis

Matlab software was used to fit out the linear equation between the properties of CR/EVA modified asphalt and modification processes. The equations are shown below:

$$y_1 = 53.2241 - 0.0044t - 0.1444h + 0.0003r \tag{1}$$

$$y_2 = 67.7222 - 0.0772t + 0.6889h - 0.0012r \tag{2}$$

$$y_3 = 9.3907 - 0.0047t - 0.0667h + 0.0002r \tag{3}$$

$$v_4 = 3.6926 - 0.0042t + 0.1889h - 0.0005r \tag{4}$$

where y_1 , y_2 , y_3 , and y_4 represent softening point, penetration, ductility, softening point difference, respectively; and *t*, *h*, and *r* represent shearing temperature, shearing time, and the shearing rate, respectively.

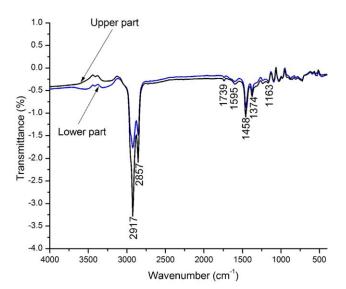


Figure 14. Infrared spectra of upper and lower parts of modified asphalt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Factor Levels Tab	ole
------------------------------	-----

	Factors					
Levels	Shearing temperature (A) (°C)	Shearing time (B) (h)	Shearing rate (A) (r/min)			
1	160	2	3750			
2	140	1.5	2500			
3	120	1	1250			

Formulae which were fitted out by Matlab software can qualitatively analyze the effects of modified processes on the properties of modified asphalt. The front coefficient of the three parameters of modified processes can conclude which is the foremost factor affecting the properties of modified asphalt, and the last factor. It can be drawn from the softening point and modification process formula: the front coefficient of shearing temperature, shearing time, and shearing rate were 0.0044, 0.1444, and 0.0003, respectively. The front coefficient of shearing time was the biggest, the second was shearing temperature, and the last was shearing rate. It can be concluded that shearing time was the foremost factor affecting the softening point of CR/EVA modified asphalt, followed by shearing temperature, and the last was shearing rate. Similarly, in accordance with the above method, from the second to the fourth formulae, it can also be drawn that in the modification process of shearing temperature, shearing time and shearing rate, shearing time was the foremost factor affecting the penetration, ductility, and softening point difference of CR/EVA modified asphalt, the second was shearing temperature and the last was shearing rate.

It can be concluded that the modification process had effect on the properties of CR/EVA modified asphalt. However, the degree of influence is different. From the size of the coefficients, it can be learned that shearing time was the foremost factor affecting the properties of CR/EVA modified asphalt, followed by shearing temperature, and the last was shearing rate. Thus, according to the degree of each modification process on the influence of modified asphalt, we can further optimize the modification process pertinently.

Table	IV.	Test	Program
-------	-----	------	---------

	_	Fac			
Test number	A		В	С	Test program
1	1	1	1	1	$A_1B_1C_1$
2	1	2	2	2	$A_1B_2C_2$
3	1	З	З	З	$A_1B_3C_3$
4	2	1	2	3	$A_2B_2C_3$
5	2	2	З	1	$A_2B_3C_1$
6	2	3	1	2	$A_2B_1C_2$
7	3	1	3	2	$A_3B_3C_2$
8	3	2	2	3	$A_3B_1C_3$
9	3	3	1	1	$A_3B_2C_1$

		Facto	rs		
Test number	A		В	С	Softening point (°C)
1	1	1	1	1	53.5
2	1	2	2	2	53.3
3	1	3	3	3	52.5
4	2	1	2	3	53.5
5	2	2	3	1	52.7
6	2	3	1	2	51.5
7	3	1	3	2	53.2
8	3	2	1	3	52.4
9	3	3	2	1	53.1
Kı	159.3	160.2	157.4	159.3	
K ₂	157.7	158.4	159.9	158.0	
Кз	158.7	157.1	158.4	158.4	
k ₁	53.10	53.40	52.47	53.10	
k ₂	52.57	52.80	53.30	52.67	
k ₃	52.90	52.37	52.80	52.80	
R	0.53	1.03	0.83	0.43	
			$R_{\rm B} > R_{\rm A} > R_{\rm C}$		

Table V. The Effect of Modified Parameters on the Softening Point

Table VI. The Effect of Modified Parameters on the Penetration

		Facto	ors		
Test number	A		В	С	Penetration (0.1 mm)
1	1	1	1	1	50.4
2	1	2	2	2	57.1
3	1	3	3	3	53.7
4	2	1	2	3	52.1
5	2	2	3	1	53.1
6	2	3	1	2	55.6
7	3	1	3	2	49.0
8	3	2	1	3	64.1
9	3	3	2	1	57.9
Kı	161.2	151.5	170.1	161.4	
K ₂	160.8	174.3	167.1	161.7	
K ₃	171.0	167.2	155.8	169.9	
k1	53.73	50.50	56.70	53.80	
k ₂	53.60	58.10	55.70	53.90	
k ₃	57.00	55.73	51.93	56.63	
R	3.40	7.60	4.77	2.83	
			$R_{\rm B} > R_{\rm A} > R_{\rm C}$		

Orthogonal Experiment Analysis

Orthogonal experiment is a method which uses orthogonal table to analyze the experiment. Through comprehensive comparison and statistical analysis, this can be achieved by a few experiments to find better production conditions, and achieve the maximum effect of the production process. Three factors (shearing time, shearing rate, and shearing temperature) and three levels (each factor has three values) are included in this experiment. The interaction between various factors are not investigated in this experiment and the table of L9 (3^4) are selected. Factor levels table is shown in Table III. And test program is shown in Table IV.



		Factor	rs		
Test number	A		В	С	Ductility (cm)
1	1	1	1	1	9.1
2	1	2	2	2	9.6
3	1	3	3	3	8.5
4	2	1	2	3	9.6
5	2	2	3	1	9.3
6	2	3	1	2	9.0
7	3	1	3	2	8.9
8	3	2	1	3	8.7
9	3	3	2	1	9.1
K ₁	27.2	27.6	26.8	27.5	
K ₂	27.9	27.6	28.3	27.5	
Кз	26.7	26.6	26.7	26.8	
k1	9.07	9.20	8.93	9.17	
k ₂	9.30	9.20	9.43	9.17	
k ₃	8.90	8.87	8.90	8.93	
R	0.40	0.33	0.53	0.24	
			$R_{\rm B} > R_{\rm A} > R_{\rm C}$		

Table	VII.	The	Effect	of Modified	Parameters	on	the Ductility	
-------	------	-----	--------	-------------	------------	----	---------------	--

Table VIII. The Effect of Modified Parameters on the Softening Point Difference

			Factors		
Test number	A		В	С	Softening point difference (°C)
1	1	1	1	1	1.2
2	1	2	2	2	2.8
3	1	3	3	3	1.8
4	2	1	2	3	1.2
5	2	2	3	1	0.8
6	2	3	1	2	1.2
7	3	1	3	2	2.8
8	3	2	1	3	3.6
9	3	3	2	1	1.3
Kı	5.8	5.2	6.0	3.3	
K ₂	3.2	7.2	5.3	6.8	
Kз	7.7	4.3	5.4	6.6	
k ₁	1.93	1.73	2.00	1.10	
k ₂	1.07	2.40	1.77	2.27	
k ₃	2.57	1.43	1.80	2.20	
R	1.50	0.97	0.23	1.17	
			$R_{\rm A} > R_{\rm C} > R_{\rm B}$		

By using the orthogonal experiments, the modification parameters affecting the properties of CR/EVA modified asphalt were analyzed. The effect of modified parameters on the softening point is shown in Table V. When any column level number is *i*, the sum of corresponding test results is K_i . S is a number that appears each level of any row ($k_i = K_i/S$). R_j represents the variance (for instance, in Table V, in the first column, $K_1 = 53.5 + 53.3 + 52.5 = 159.3$, S = 3,

 $k_1 = 159.3/3 = 53.10$). The greater the R_j is, the larger the factors influencing the test index is. According to the size of the R_j primary and secondary order of each factor can be determined. The effect of modified parameters on the penetration and ductility are shown in Tables VI and VII. As can be seen in Tables V–VII, shearing time was the foremost factor affecting the softening point of CR/EVA modified asphalt, the second was shearing temperature and the last

was shearing rate. The conclusions were consistent with the results of formulae which were fitted out by Matlab software.

The effect of modified parameters on the softening point difference is shown in Table VIII. As can be seen in Table VIII, shearing temperature was the foremost factor affecting the softening point difference of CR/EVA modified asphalt, the second was shearing rate and the last was shearing time. It is not consistent with the above results. The reasons maybe as follows: different order of selection factors and different order of selection levels may be influence the results.

CONCLUSIONS

In this study, with the mass fraction of 5% of CR and the mass fraction of 2% of EVA modified asphalt, the effects of the modification process on the properties of CR/EVA modified asphalt were discussed.

Softening point, penetration, ductility, and softening point difference of CR/EVA modified asphalt were tested. It can be concluded that the properties of CR/EVA modified asphalt were greatly improved. Softening point raised over 6 °C, penetration at 25 °C reduced 2 mm, and ductility at 5 °C increased more than four times, respectively. The influence of shearing time, shearing temperature, and shearing rate on the properties of CR/EVA modified asphalt was studied. When temperature was 140 °C, time was 1.5 h, and rate was 3750 r/min, the properties of CR/EVA modified asphalt were the best. A segregation experiment was applied to evaluate the storage stability of CR/ EVA modified asphalt. The softening point difference was almost less than 2.5 °C. It can be seen that the compatibility of modifiers and asphalt improved to a certain extent.

Matlab software was employed to fit out the linear equations between softening point, penetration, ductility, softening point difference and shearing rate, shearing time, and shearing temperature. It was learnt that the modification process had effect on the properties of CR/EVA modified asphalt. The shearing time was the foremost factor affecting the properties of CR/EVA modified asphalt, followed by shearing temperature, and the last was shearing rate. The conclusions which were fitted by orthogonal experiment were basically consistent with the results of formulae which were fitted out by Matlab software.

ACKNOWLEDGMENTS

The authors acknowledge the financial supports provided by the National Natural Science Foundation of China (Grant No. 51172180 and 51372200), Program for New Century Excellent Talents in University of Ministry of Education of China (Grant No. NCET-12-1045).

REFERENCES

- 1. Navarro, F. J.; Partal, P.; Martinez-Boza, F.; Valencia, C.; Gallegos, C. *Chem. Eng. J.* **2002**, *89*, 53.
- 2. Lesueur, D. Adv. Colloid. Interface Sci. 2009, 145, 42.
- 3. Navarro, F. J.; Partal, P.; Gallegos, C. Eur. Polym. J. 2005, 41, 1429.
- 4. Yildirim, Y. Constr. Build. Mater. 2007, 21, 66.
- Polacco, G.; Berlincioni, S.; Biondi, D.; Stastna, J.; Zanzotto, L. *Eur. Polym. J.* 2005, 41, 2831.
- Xiao, F. P.; Amirkhanian, S. N.; Shen, J. N. Constr. Build. Mater. 2009, 23, 1028.
- 7. Zhang, H. L.; Yu, J. Y.; Wu, S. P. Constr. Build. Mater. 2012, 27, 553.
- 8. Zhu, J. Q.; Bjorn, B.; Kringos, N. Eur. Polym. J. 2014, 54, 18.
- 9. Golzar, K.; Jalali-Arani, A.; Nematollahi, M. Constr. Build. Mater. 2012, 37, 822.
- Liu, H. Y.; Chen, Z. J.; Wang, W.; Wang, H. N.; Hao, P. W. Constr. Build. Mater. 2014, 67, 225.
- 11. Liang, R. Y.; Lee, S. Transp. Res. Rec. J. Transp. Res. Board 1996, 1530, 7.
- 12. Wang, H. N.; Dang, Z. X.; You, Z. P.; Cao, D. W. Constr. Build. Mater. 2012, 35, 281.
- 13. Li, X.; Jian, C.; Kang, S. J. Constr. Build. Mater. 2015, 75, 169.
- 14. Yin, J. M.; Wang, S. Y.; Lv, F. R. Constr. Build. Mater. 2013, 49, 712.
- 15. Huang, B. S.; Shu, X. Constr. Build. Mater. 2014, 67, 217.
- 16. Bahia, H. U.; Davies, R. J. Assoc. Asphalt Paving Technol. 1994, 63, 414.
- 17. Liu, S. T.; Cao, W. D.; Fang, J. G.; Shang, S. J. Constr. Build. Mater. 2009, 23, 2701.
- Navarro, F. J.; Parta, IP.; Martinez-Boza, F.; Gallegos, C. Fuel 2004, 83, 2041.
- 19. Zhang, F.; Yu, J. Y.; Wu, S. P. J. Hazard. Mater. 2010, 182, 507.
- 20. Zhang, F.; Yu, J. Y.; Han, J. Constr. Build. Mater. 2011, 25, 129.
- Liang, M.; Xin, X.; Fan, W. Y.; Luo, H.; Wang, X. B.; Xing, B. D. Constr. Build. Mater. 2015, 74, 235.
- 22. Ye, F.; Yin, W.; Lu, H. Constr. Build. Mater. 2015, 79, 397.
- 23. Fang, C. Q.; Liu, P.; Yu, R. E.; Liu, X. L. Constr. Build. Mater. 2014, 54, 320.
- 24. JTJ T 0661-2000. Standard Test Method for Segregation of Polymer Modified Asphalt.
- 25. Ana, M. R.; Juan, G.; Ignacio, P.; Alice, B.; Felice, G. Constr. Build. Mater. 2014, 53, 460.

