INFLUENCE AND MECHANISM OF ULTRAVIOLET AGING ON BITUMEN PERFORMANCE

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ABSTRACT

Ultraviolet (UV) and thermal aging are two quite different types of aging. This study experimentally compares UV aging with thermal aging of several bituminous binders. Bitumen was evaluated with respect to its changes in physical and rheological properties. The results show that bitumen has different sensitivities to UV and thermal radiation. Penetration values, softening point and ductility of UV-aged bitumen are not the same as those in thermally aged bitumen. Rheological indices also reveal that UV aging and thermal aging have different influences on bitumen. The low-temperature property degraded remarkably due to UV aging. This paper also explains the mechanism of aging behaviour using infrared spectroscopy and chemical component investigation, and points out that aromatics and resins are the crucial chemical components for the anti-UV aging ability of bitumen.

1. INTRODUCTION

Bitumen is easily aged in the field, especially when exposed to thermal and/or UV radiation conditions. UV and thermal aging are two quite different types of aging. However, the current bitumen performance evaluation system gives little consideration to UV aging.

Because of the differences in air composition and the length of the solar radiation path between plateaus and low-altitude plains, plateaus have unique climatic and environmental features due to their more intense radiation, longer daylight hours, and especially their much higher UV percentage, which ranges from 20% to 25% of the total solar light. This is five times more than that on plains (Zhou, 1986 and Xiao, 2003). Such intense UV radiation causes serious aging of bitumen, which influences its performance. As a result, the durability of the pavement decreases. Therefore it is important to study specifically the influence of UV radiation on bitumen performance.

In this study the influence of UV aging on bitumen performance was investigated using special aging acceleration equipment and processes designed to simulate UV aging of bitumen in the field (Tan, 2003),

2. EXPERIMENTAL

2.1 Basic physico-chemical properties of the materials

In order to study the influence of UV radiation on bitumen properties and to compare differently aged samples, three types of base bitumen (denoted as A, B, and C) from different sources but with the same penetration grade, and two polymer-modified asphalt binders (M-SBS, M-SBR) were studied. Their basic physical and chemical properties are summarised in Table 1.

Each type of bitumen listed below was assigned an identification code that provides information on the source and physical state of the material. The identification code consists of two parts. The first part indicates the source of the bitumen, e.g. A, B, M-SBS. The second part identifies the aging state, i.e. original, thermal or UV (O, T or U). Thus A-O means original bitumen sample from A and M-SBS-T means a thermally aged M-SBS sample.

Table 1. Physico-chemical properties of original bitumen

Bitumen variety		A-O	B-O	C-O	M-SBS-O	M-SBR-O
Penetration (25 °C; 0.1 mm)		79	82	81	96	99
Ductility (10 °C; cm)		52.7	74.3	45.3	167.5	165
Softening points (°C)		46.3	42.6	45.9	61.9	71.7
Chemical component (%)	Asphaltene (At)	1.5	4.7	10.3	—	—
	Aromatics (Ar)	31.5	24.3	46.3	—	—
	Saturate (S)	33.6	35.1	23	—	—
	Resin (R)	33.5	35.9	20.5	—	—

2.2 Artificial UV aging procedures

A rolling thin-film oven (RTFO) was used in this study for thermal aging. The ultraviolet radiation equipment mentioned by Tan (2003) was also used. The bitumen was exposed to UV at a temperature of 73 °C for 9 hours, so that the radiation energy was equivalent to the total energy received over a period of 5 months in Tibet.

2.3 Bitumen performance tests

2.3.1 DSR test

This was conducted with a Gemini-150 rheometer in a parallel-plate configuration with a gap of 2 000 μm at 0 °C. The stress was 1.5×10^4 Pa at a frequency of 0.1 rad/s.

2.3.2 BBR test

The AASHTO MP5 BBR test method was used to determine the performance of the original and the aged bitumen at low temperature. The test temperature was -12 °C.

2.3.3 Chemical component separation methods

The Corbett ASTM D-4124 method was used to separate the bitumen into four fractions, namely asphaltene, resin, aromatics and saturates.

3. RESULTS AND DISCUSSION

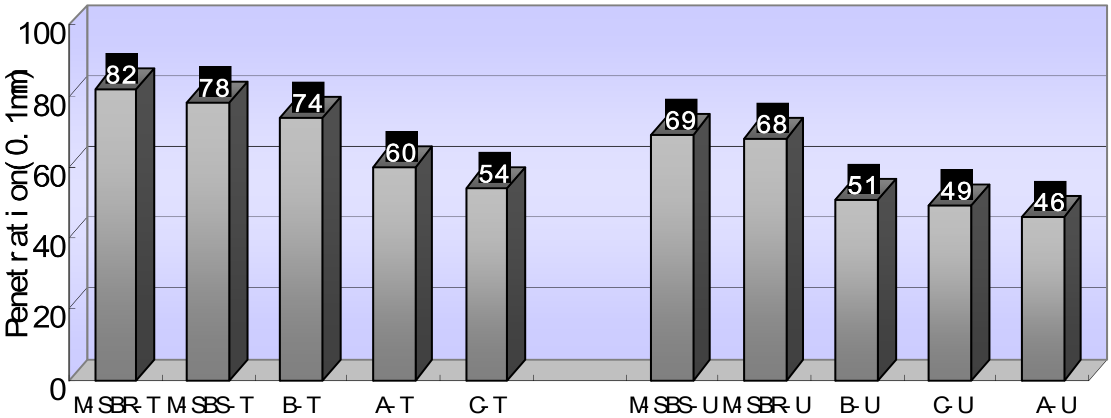
3.1 Comparison of the physical properties of aged bitumen

Table 2 presents the physical indices of original, thermal and UV-aged bitumen. After UV aging, the penetration and ductility values decreased while the softening points increased.

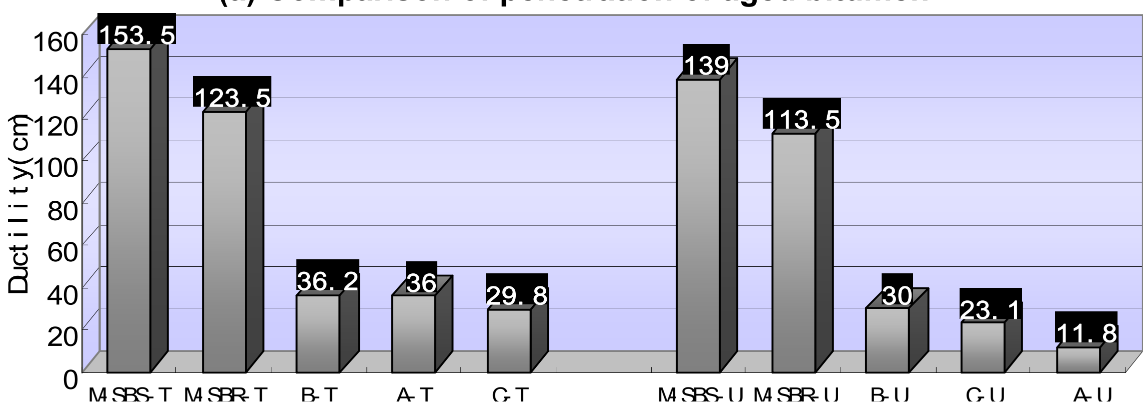
Table 2. Physical indices of thermally and UV-aged bitumen

Bitumen variety		A	B	C	M-SBS	M-SBR
Penetration (25 °C; 0.1 mm)	Original bitumen (Po)	79	82	81	96	99
	Thermal aging (Pt)	60	74	54	78	82
	Ultraviolet aging (Pu)	46	51	49	69	68
Ductility (10 °C; cm)	Original bitumen (Do)	52.7	74.6	45.3	167.5	165
	Thermal aging (Dt)	36	36.2	29.8	153.5	123.5
	Ultraviolet aging (Du)	11.8	30	23.1	139	113.5
Softening point (°C)	Original bitumen (So)	46.3	42.6	45.9	61.9	71.7
	Thermal aging (St)	48.1	47.3	50	60.7	66
	Ultraviolet aging (Su)	56.7	48.0	54.2	64.9	67.3

To compare the influences of thermal and UV aging on the properties of bitumen, penetration and ductility were listed in order as shown in Figure 1:



(a) Comparison of penetration of aged bitumen



(b) Comparison of ductility of aged bitumen

Figure 1. Comparison of physical indices of thermally and UV-aged bitumen

From the orders shown above, it can be seen that even for the same type of bitumen, different samples have quite different sensitivities and anti-aging resistance to UV radiation and thermal aging. Differences are also noticeable among different bitumen types.

Figure 2 shows the changes to the physical indexes of bitumen A and B caused by aging. A is more UV radiation sensitive because larger changes of the physical indices can be seen. Its penetration decreased by 42%, the ductility decreased by 77.6%, and the softening points increased by 22.6%, showing poor anti-UV ability. On the contrary, B is not very sensitive to UV but is more thermally sensitive, as only small changes caused by UV radiation but great changes in ductility and softening points caused by thermal aging can be seen.

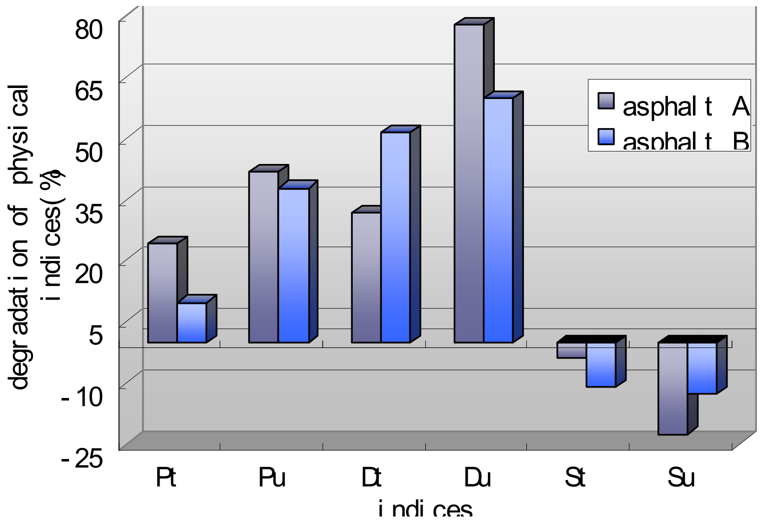


Figure 2. Degradation rates of physical indices of aged bitumen

The variations in the physical indices indicate that bitumen has different sensitivities to thermal and UV aging. Therefore an evaluation based on thermally aged bitumen does not truly reflect bitumen's anti-UV ability.

3.2 Changes in the rheological properties of aged bitumen

As bitumen is a typical viscoelastic material, the ratio between viscosity and elasticity plays a key role in its rheological properties. In this study the DSR and BBR tests were used to investigate the influence of UV radiation on rheological properties.

3.2.1 DSR test indices

The rheological properties of bitumen are well reflected by the loss modulus G'' and phase angle δ at low / intermediate temperature. The energy dissipated in flow deformation to resist loading is expressed as loss modulus G'', and δ is an index of the ratio between viscosity and elasticity. Lower values of G'' and δ are undesirable as they indicate degradation of rheological properties. . The G'' and δ values of the original and aged bitumen are presented in Table 3. Decreases of these two indices reveal that UV aging changes the viscoelastic character of bitumen and increases elasticity (decreases viscosity). As a result, the flow property drops.

Table 3. Loss modulus (MPa) and phase angle (°)

Class	A		B		C		M-SBS		M-SBR	
	δ	G″	δ	G″	δ	G″	δ	G″	δ	G″
Original bitumen	20.3	1.19	13.1	0.97	13.2	0.96	30.8	1.30	32.1	1.32
Thermal aging	18.9	1.03	12.7	0.99	11.2	0.85	30.3	1.30	31.7	1.37
Ultraviolet aging	13.8	0.8	12.0	0.92	10.0	0.74	28.4	1.21	18.9	1.18

3.2.2 BBR test indices

The stiffness (***S***) and the slope m-value (***m***) at 60th s were used to evaluate low temperature performance (Zhao, 1997; Aroon, 2002). The results are shown in Table 4, where the effects of UV aging of bitumen can clearly be seen in the variations of ***S*** and ***m***. It can be observed that ***S*** increased and ***m*** decreased during UV aging. The variation tendencies of ***S*** and ***m*** imply an increase in elastic response, a decrease in viscosity and a drop in rheological properties after UV aging at low temperature.

Table 4. Stiffness (S) and m values

Class	A		B		C		M-SBS		M-SBR	
	S	m	S	m	S	m	S	m	S	m
Original bitumen	45.8	0.54	120	0.5	76.6	0.39	90.3*	0.42*	119*	0.44*
Thermal aging	62.5	0.9	146	0.45	112	0.43	99*	0.41*	96.1*	0.48*
Ultraviolet aging	70.3	0.47	152	0.45	141	0.39	30.8	0.49	52.3	0.39

Note: *the test temperature was -18°C

From the results of the DSR and BBR tests, it was found that the changes in rheological properties during UV aging were not consistent with those during thermal aging. After UV aging, the *G*″, *δ*, ***S*** and ***m*** values of M-SBS were better than of the values for M-SBR, contrary to the results of M-SBS and M-SBR after thermal aging. The modified asphalt M-SBS and M-SBR exhibit noticeable differences in their UV and thermal aging properties. A comparison of the loss modulus of aged bitumen is shown in order in Figure 3.

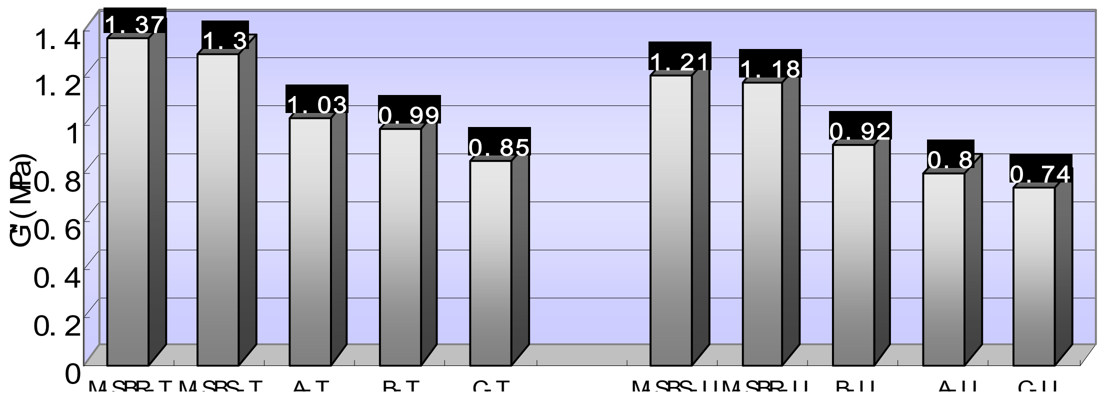


Figure 3. Comparison of loss modulus of thermally and UV-aged bitumen

The changes of the rheological indices indicate that UV and thermal aging have different influences on bitumen. An evaluation based on thermally aged bitumen may not exactly reflect the effects of UV aging, and there will be some limitations on the substitution of UV aging by thermal aging.

3.3 Relationship between UV aging behaviour and chemical components

To explain the variations of physical and rheological properties after UV aging, the chemical components of three types of base bitumen were investigated.

Aging is a series of complicated and mutually related reactions of the components of bitumen. The transformation trend between components can be briefly expressed as follows: aromatics transform into resin, and resin transforms into asphaltene at the same time (Liu, 2001). As the reactants, saturates, aromatics or resin transform and interact with each other, it becomes very hard to estimate the degree of the aging reaction simply from the changes of one or several parts of the components. Contrary to this, asphaltene is a product of the aging reaction, and the amount of asphaltene increases stably at a constant rate. Therefore it is feasible to evaluate the degree of aging of bitumen by determining the variation of the density of asphaltene (Jin, 2001 and Peterson, 1993).

Based on the theory mentioned above, the asphaltene content was compared before and after aging (Table 5). The asphaltene content of A and C after UV aging was significantly higher than it was after thermal aging, with an increase of 40% and 26.2% after UV aging respectively. However, B shows an opposite aging effect on the amount of asphaltene, being more susceptible to thermal aging than to UV radiation.

Table 5. Chemical components of original and aged bitumen

Chemical components	A-O	A-T	A-U	B-O	B-T	B-U	C-O	C-T	C-U
Saturates (symbol: S)	31.5	30.0	29.9	35.9	34.7	34.6	23	19	18.7
Aromatics (symbol: Ar)	33.6	24.5	23.2	35.1	30.9	30.7	45.3	43.5	44.6
Resin (symbol: R)	33.5	43.6	44.9	24.3	27.4	28.1	20.5	25.8	23.7
Asphaltene (symbol: At)	1.5	1.8	2.1	4.7	6.9	6.6	10.3	11.7	13

From the point of view of the total amount of resin and asphaltene, the aged bitumen can be ordered as: B-U < C-U < A-U (Figure 4), and their physical properties can be ordered from high to low as B-U > C-U > A-U. The consistency between these two orders indicates that UV aging has an inverse effect on colloidal stability, and therefore decreases the physical properties of bitumen.

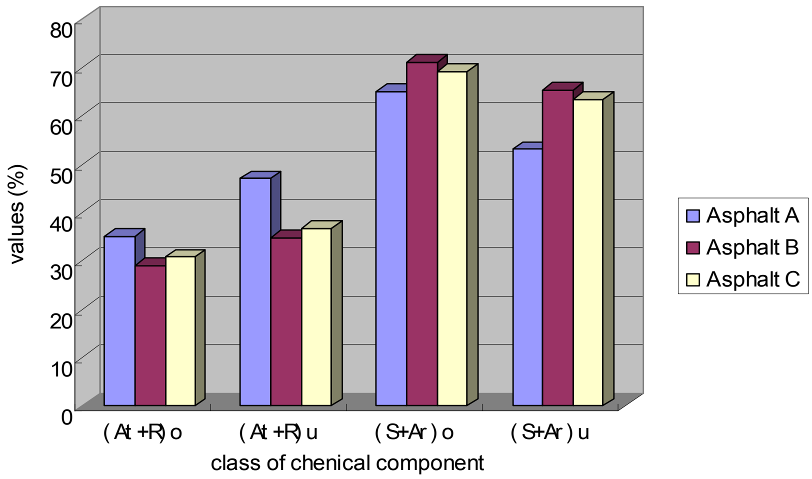


Figure 4. Content of chemical components of original vs. UV-aged bitumen

Note: (At+R)o, (At+R)u, (S+Ar)o and (S+Ar)u stand for the chemical components of asphaltene and resin or saturates and aromatics of **o**riginal or **U**V-aged bitumen

Saturates and aromatics are classified together as the softening fraction such as gelatin in bitumen, while resin and asphaltene are classified as the hardening fraction which causes thickening. The relationship between the softening and hardening fractions has a good correlation with the variation rate of the DSR indices (shown in Figure 5).

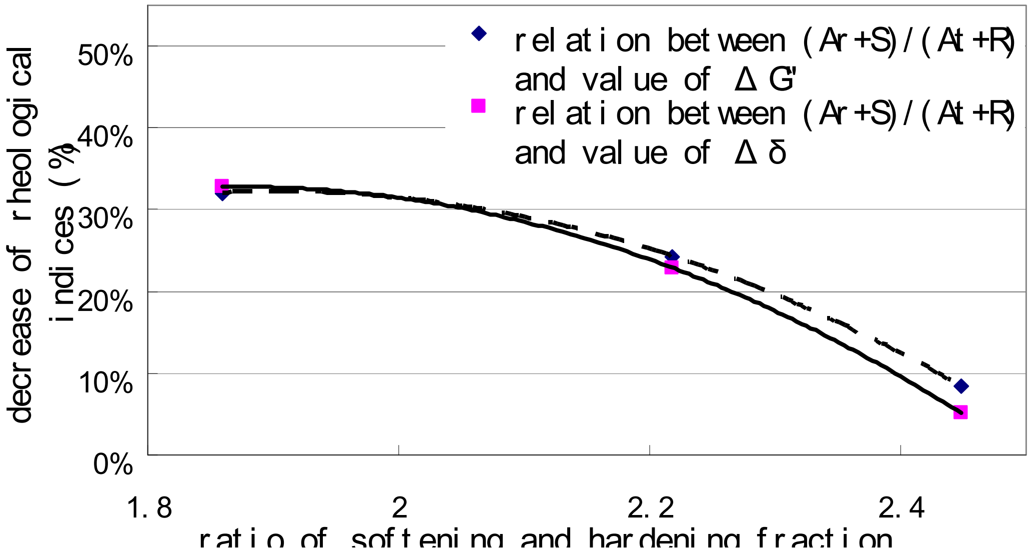
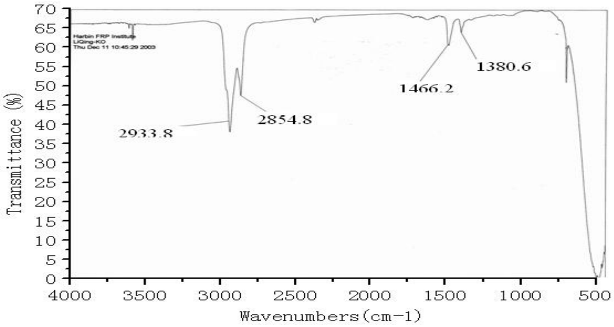


Figure 5. Regression curve of (Ar+S)/ (At+R) vs. degradation rate of *G″* and *δ*

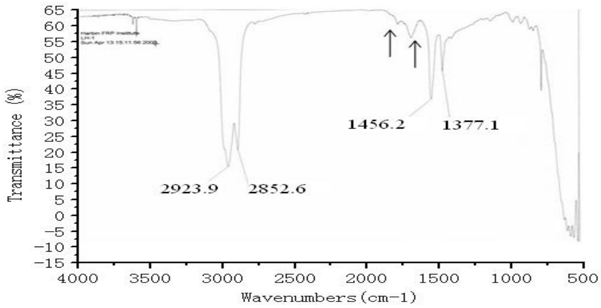
Since A-O has the smallest content of the softening and hardening fractions, the *G″* and *δ* values of A-U decrease rapidly, but B-O and C-O have a higher content, so the *G″* and *δ* values of B-U and C-U dropped only slightly, suggesting that the rheological properties were basically maintained. Essentially, the chemical components and their transformations of bitumen when exposed to UV radiation reveal an internal mechanism of the aging action and its influences on performance.

3.4 Study of the UV aging mechanism

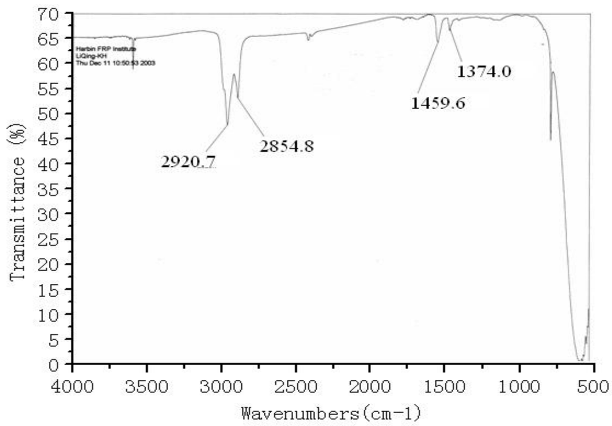
The mechanisms of UV radiation aging and thermal aging differ in the initiation process. Thermal oxidation is caused by polymer chemical bond thermal decomposition, while the initiation process of UV aging is such that some chromophores absorb UV radiation, and then transform from the ground state to the excited state, thus inducing the breaking of chemical bonds (Wu, 2003). This study investigated the changes of inner groups using infrared (IR) spectroscopy. Based on the results of previous experiments, A and B were chosen as two opposite types of bitumen for the IR spectra test because of their different sensitivities to UV radiation, as shown in Figure 6.



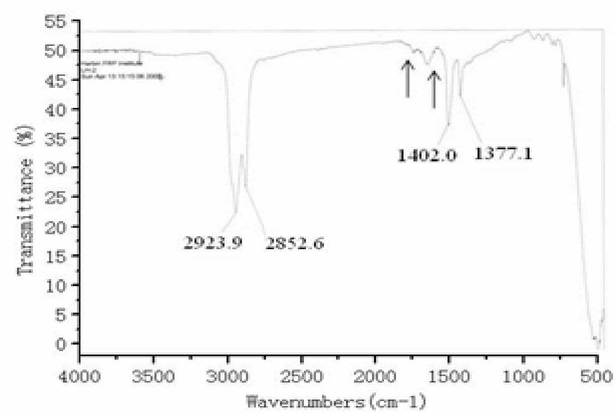
(a) IR Spectra of A-O



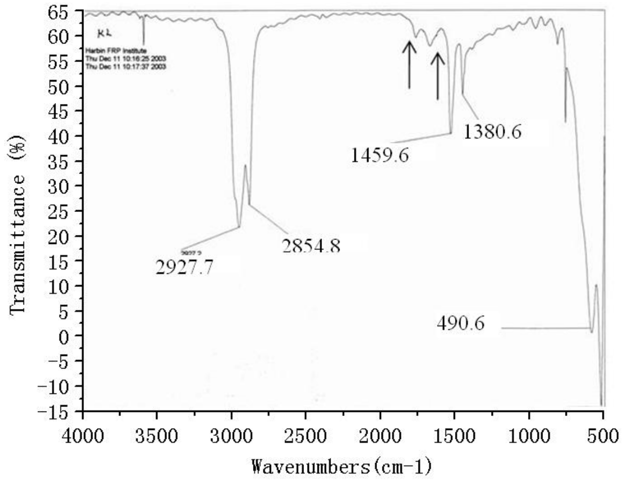
(b) IR Spectra of B-O



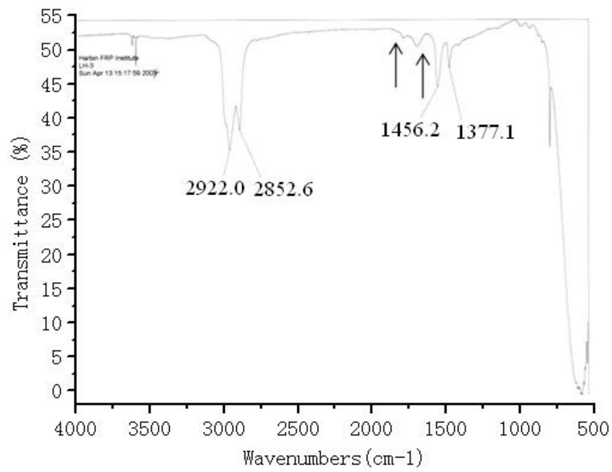
(c) IR Spectra of A-T



(d) IR Spectra of B-T



(e) IR Spectra of A-U



(f) IR Spectra of B-U

Figure 6. Infrared (IR) spectra of bitumens A and B

Zhang (2001) pointed out that the changes on absorption regions at 3 436 cm^{-1}, 1 700 cm^{-1} and 1 600 cm^{-1} in the IR spectra are mainly due to photo-oxidation (Zhang, 2001). The absorption variations of $c = o$ elongation at 1 700 cm^{-1} are best used to observe the aging reaction since there is no other functional group disturbing this band. The absorption peak of $c = o$ elongation is closely consistent with the extent of the aging reaction. The higher the absorption peak, then the greater the degree of aging of bitumen.

Figure 6 (a), (c) and (e) are the IR spectra of bitumen A. There are two absorption bands (shown by the arrows in (e)) that do not show up after thermal aging. The IR spectrum also displays very significant absorption of $c = o$ and O-H at 1 600 cm^{-1} and 1 700 cm^{-1} due to carbonyl and/or carboxyl groups. The absorption band at 1 700 cm^{-1} proves that some photo-oxidation reactions occurred in the components of A, indicating that A is more sensitive to UV radiation. The 1 700 cm^{-1} absorption band of B remained through the aging process and was reduced gradually by both thermal and UV aging (Figure 6(b), (d) and (f)). This implies that B has less sensitivity and better anti-UV ability. The IR spectra give the inherent reason for the difference in the anti-UV performance of A and B in which the degree of the aging reaction is compared. This was reflected by the changes in absorption peaks.

The IR spectrum analysis shows that carbonyl plays a key role in UV aging. The carbonyl content and its transformation are the crucial conditions for the degree of the photo-oxidation reaction. Carbonyl is converted from naphaltenes during oxidation, and naphaltenes are mostly present in aromatics and resin. Therefore aromatics and resin are two crucial components of bitumen. The sequence of the total amount of aromatics and resin in original bitumen is A>C>B (Figure 5), which is consistent with both aging and the degree and degradation ratios of the physical properties of UV-aged bitumen.

4. CONCLUSIONS

This paper presents a study of the influence of UV aging on bitumen performance. Changes in the physical and rheological properties of bitumen were investigated by experiments such as penetration, ductility, softening points, DSR and BBR, and comparisons of sensitivities to thermal and ultraviolet radiation were made. The transformation of chemical components during ultraviolet aging was also observed and the influence of UV aging on bitumen performance was explained from this perspective. Based on these investigations, some conclusions can be drawn as follows:

Ultraviolet and thermal aging have quite different influences on bitumen performance. The results of the experiments indicate that UV aging has an obvious effect on the physical and rheological properties of bitumen. Most bitumen has different sensitivities to thermal and UV radiation. Evaluations based on thermally aged bitumen do not truly reflect the influences of ultraviolet aging, and there are some limitations on the substitution of ultraviolet with thermal aging.

The transformations that take place in the chemical components during UV aging are related to the changes in properties. There is good correlation of the ratio between softening and hardening fractions and the changes in the rheological indices with UV aging.

Different types of bitumen with the same penetration grade but different refinements have quite different anti-UV abilities. This paper explains the aging behaviour mechanism using IR spectrum analysis and investigation of the chemical components, and points out that the differences in the extent of the aging reaction are due to the difference in aromatics and resin content, which are two crucial components in the anti-UV ability of bitumen..

5. ACKNOWLEDGMENTS

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