Journal of Southeast University (English Edition) Vol. 24, No. 4, pp. 503 – 507 Dec. 2008 ISSN 1003—7985

Anti-ultraviolet aging tests of asphalts adapting to environment in Tibetan Plateau of China

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Abstract: Ultraviolet (UV) aging is one of the main factors which cause premature damage of asphalt pavements in the Tibetan Plateau, China. According to the measured levels of UV radiation, aging tests of styrene-butadiene rubber (SBR) asphalts with different contents of three anti-UV-aging agents including nano-TiO_2, CeO_2 and carbon black are performed. Common indices, which include retained penetration after thin film oven tests (TFOT) and softening point, and strategic highway research program (SHRP) indices of aged asphalts are evaluated. Infrared absorption spectral analysis is performed on asphalt specimens with 0. 8% carbon black which have been aged for different aging times (500, 1000 and 1 500 h). By grey incidence analysis, the optimal contents of anti-UV-aging agents are determined. The results show that TiO_2 and CeO_2 are not only good UV absorbing or shielding agents, but also strong oxidants. Carbon black is a good anti-UV-aging agent, and its optimal content is about 0. 8% of asphalt weight. UV aging of asphalt mainly occurs in the early stages of aging. The longer the aging time, the more severe the aging of asphalt.

Key words: ultraviolet (UV) aging; agent; carbon black; infrared absorption spectral analysis; grey incidence analysis

Because of its low latitude, high altitude and clear air, the Tibetan Plateau is the area with the largest solar radiation energy in China (see Tab. 1). The annual average solar radiation energy is about 2 512 to 3 350 MJ/m^2. The solar ultraviolet (UV) radiation is also high, and the radiation level in the Tibetan Plateau is three times that of other plain areas at similar latitudes[1]. The annual ultraviolet radiation energy is 361. 9 MJ/m^2. UV radiation accelerates asphalt aging of asphalt pavements in the Tibetan Plateau and causes premature damage. Thus, anti-UV-aging tests of asphalt are of great significance.

Tab. 1 Annual solar radiation energies of different areas in China

Observation station	Latitude	Annual solar radiation/ (MJ·m^{-2})
Rongbu Temple(Tibetan Plateau)	31°25′	8 769
Shiquan River(Tibetan Plateau)	32°30′	8 102
Lhasa city(Tibetan Plateau)	29°42′	7 924
Beijing city	39°48′	5 200
Wuhan city	30°38′	4 711
Shanghai city	31°07′	4 573
Chongqing city	29°31′	3 499

Received 2008-03-26.

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Citation: Liao Gongyun, Huang Xiaoming, Ba Sang Dunzhu. Anti-ultraviolet aging tests of asphalts adapting to environment in Tibetan Plateau of China[J]. Journal of Southeast University (English Edition), 2008, 24(4): 503 – 507.

1 Background

Asphalt is one of several organic polymer materials. Anti-UV aging performance of asphalt can be improved by adding some agents. In terms of organic polymer materials[2], these agents can be divided into three types. The first type is a light-shielding agent, such as nano-TiO_2, CeO_2 and carbon black. After absorbing ultraviolet radiation energy, such material can transform the energy into heat energy and then disperse, or directly reflect ultraviolet energy away. The second type is a UV-absorbing agent, which can have strong UV absorption and can be dissolved in asphalt, selectively absorbing harmful ultraviolet bands, and transforming them into vibration energies or sub-radiation energies, such as fluorescence and phosphorescence, which are not harmful to the material itself, and asphalt material can be immune from UV damage. The third type is a quenching agent, which can transform instantaneously excitation energies of excited molecules under UV radiation by molecular energy transmission, and allow molecules to return to their stable states.

Chiu investigated the changes of common indices of ordinary asphalts by different aging methods including TFOT, PAV and UV, and infrared absorption spectral analysis was also conducted[3]; Zhao et al. studied the anti-UV-aging effects of nano-CeO_2 with different contents[4-5] and considered that the optimal content of nano-CeO_2 is 0. 8%. Dong et al. researched the effects of different anti-UV-aging agent contents on asphalt anti-aging performance[6-7]. Jiang et al. discussed common indices, such as penetration, softening point, ductility and viscosity of SBR/SBS modified asphalt, by TFOT and UV aging test[8]. Wu et al. investigated anti-UV-aging performance of SBR mixtures by using a high-pressure ultraviolet mercury lamp[9]. Zhou et al. considered the aging resistance properties of PP/TiO_2 nanocomposites[10]. None of the above researches compares the effects of different nano-materials on the UV resistance of asphalts.

2 Ultraviolet Test of Asphalt with Anti-UV Agents

To improve the anti-UV-aging performance of asphalts, three anti-UV-aging agents are tested including nano-TiO_2, CeO_2 and carbon black.

2. 1 Test materials

Asphalt material: styrene-butadiene rubber (SBR) modified asphalt.

Anti-UV-aging agent: TiO_2, CeO_2 and carbon black; all are nano-materials.

UV radiation energy level: assume that an indoor UV radiation of one month (720 h) is equal to that of annual outdoor UV radiation energy (361. 9 MJ/m^2). So, the UV radiation energy level is 0. 503 MJ/m^2 per hour.

2. 2 Production of asphalt film smears

While mixing TiO_2, CeO_2 or carbon black with asphalt, the stirring temperature should be controlled between 160 and 170 °C. If the stirring temperature is too low, asphalt viscosity will be too large to disperse TiO_2, CeO_2 or carbon black powders into the asphalt. But too high a stirring temperature will cause serious aging of asphalt.

After heating and stirring asphalt within the above temperature range, a certain number of powder materials, TiO_2 or CeO_2 of 0. 5%, 1. 0%, 1. 5% or carbon black of 0. 5%, 0. 8%, 1. 2%, is added slowly into liquid asphalt. To disperse these powders uniformly into asphalt, a stirring time of 120 min is needed at a stirring speed of 1 200 r/min. Finally, the mixed asphalt is smeared onto a special paper, and then 0. 03 cm asphalt film smears are formed.

2. 3 UV aging of asphalt

Placing asphalt film smears into a UV-aging tester (see Fig. 1(a)), the aging test is undertaken at 45 ℃. Fig. 1(b) illustrates some samples of UV-aged asphalt film smears.

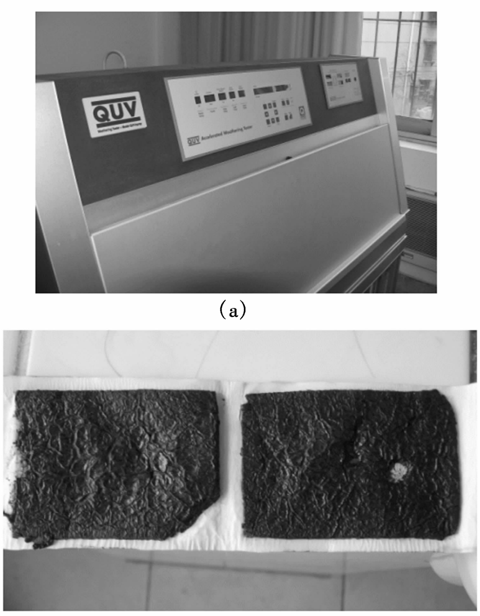

Fig. 1 UV-aging tester and some samples of UV-aged asphalt film smears. (a) QUV tester; (b) Samples of UV-aged asphalt film smears

3 Analysis of Common Indices and SHRP Indices of UV-Aged Asphalts

3. 1 Analysis of common indices

3. 1. 1 Changes of retained penetration after TFOT

Fig. 2(a) lists the relationships between retained penetration after TFOT of UV-aged asphalts with TiO_2 and aging time. It can be seen that the anti-UV-aging performance of asphalt with only 0. 5% TiO_2 is somewhat better than that of unmodified asphalt. But the anti-aging performance of asphalt with 1. 0% or 1. 5% TiO_2 is poor. The more the content of TiO_2, the worse the anti-aging performance of asphalt. This is because TiO_2 is not only a strong UV-absorbing agent, but also a good optical catalyst. Some strong oxides produced under UV radiation can greatly reduce the anti-UV-aging performance of modified asphalt.

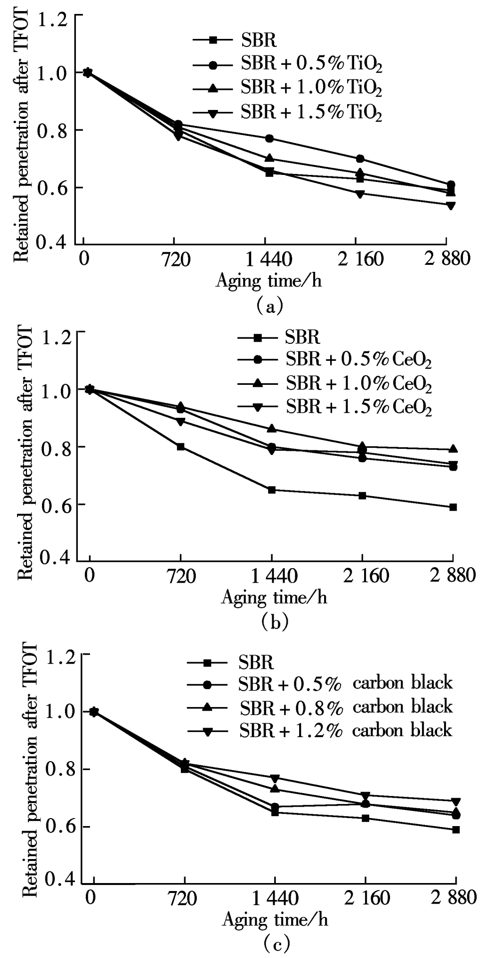

Fig. 2 Relationships between retained penetration of UV-aged asphalts and aging time. (a) TiO_2; (b) CeO_2; (c) Carbon black

Relationships between retained penetration after TFOT of UV-aged asphalts with CeO_2 and aging time are shown in Fig. 2(b). It can be seen that the anti-UV-aging performance of asphalts with CeO_2 is improved. The retained penetration of asphalt with 1. 0% CeO_2 reaches the maximal value, and with 1. 5% CeO_2 the value decreases again. This is because CeO_2 is not only a UV absorbing and shielding agent, but also an oxidant. Some oxides produced under UV radiation can accelerate oxidation of asphalt.

Retained penetration after TFOT of UV-aged asphalts with carbon black for different aging times can be found in Fig. 2(c). It can be seen that with the increase of carbon black content, retained penetrations of asphalts are improved. When carbon black content reaches 1. 2%, retained penetration also reaches the maximal value; that is, anti-aging performance is at its best. This is because carbon black is a good UV absorbing agent without oxidation, and can absorb light oil in asphalt. Thus, carbon-black-modified asphalt has good anti-UV-aging performance.

3. 1. 2 Changes of softening point

Softening points of UV-aged asphalts with three anti-UV-aging agents for different aging times are illustrated in Fig.

3. It can be seen that softening points of asphalts increase with aging time. The change of the softening point of modified asphalt with 1. 5% TiO_2 is the largest. When the agent content reaches a certain value, the oxidation of the asphalt will increase greatly. But a change in the softening point of asphalt with 1. 2% carbon black is significantly lower than that of the other two modified asphalts. These show that, carbon black has good UV absorption and shielding properties, but it has no oxidation.

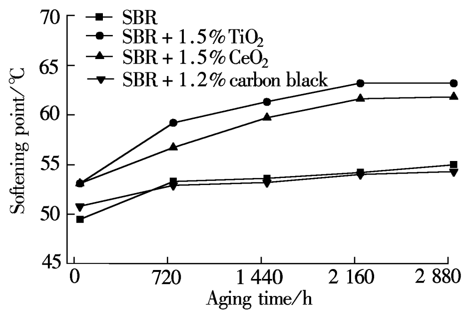

Fig. 3 Relationships between softening point of UV-aged asphalts and aging time

3. 2 Analysis of SHRP indices

3. 2. 1 Brookfield rotary viscosity

For different aging times, Brookfield rotary viscosity (135 ℃) of asphalt with different contents of three anti-UV-aging agents are shown in Fig. 4. It can be seen that as the aging time and the contents of the three anti-UV-aging agents increase, the Brookfield rotary viscosities of all the modified asphalts increase. The change in asphalt viscosity with TiO_2 is larger than that with carbon black. When carbon black content reaches 1. 2%, Brookfield rotary viscosity changes only 14. 8%. It shows that the optimal content of carbon black is 0. 8%.

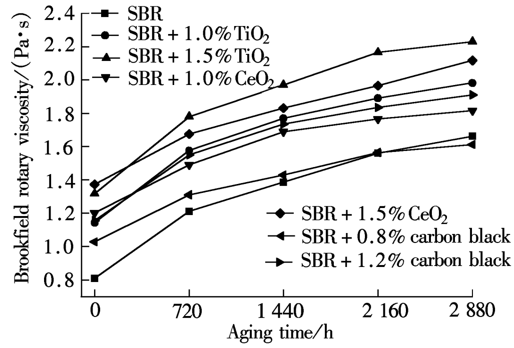

Fig. 4 Relationships between Brookfield rotary viscosity of asphalt and aging time

Tab. 2 shows changed Brookfield rotary viscosity (135 ℃) of asphalts with three anti-UV-aging agents. It can be seen that, for SBR asphalt with 1. 0% TiO_2, its incremental rotary viscosity results not only from aging time, but also from TiO_2 itself. Contrarily, for the other two asphalts, their incremental rotary viscosity results mainly from aging time, not from CeO_2 or carbon black.

Tab. 2 Changed Brookfield rotary viscosity of asphalts with anti-UV-aging agents Pa·s

Aging time/h	SBR	SBR + 1. 0% TiO_2		SBR + 1. 0% CeO_2		SBR + 0. 8% carbon black	
	Measured	Measured	Changed	Measured	Changed	Measured	Changed
0	0. 811	1. 145	0. 334	1. 203	0. 392	1. 028	0. 217
720	1. 212	1. 576	0. 364	1. 491	0. 279	1. 311	0. 099
1 440	1. 386	1. 771	0. 385	1. 691	0. 305	1. 429	0. 043
2 160	1. 56	1. 892	0. 332	1. 767	0. 207	1. 564	0. 004
2 880	1. 664	1. 983	0. 319	1. 817	0. 153	1. 613	-0. 051

3. 2. 2 $G^*/\sin\delta$

It can be seen from Fig. 5 that, $G^*/\sin\delta$ of all modified asphalts increases with aging time; that is, high-temperature performance is improved. The anti-UV-aging performance of asphalt with 1% CeO_2 is better than that with 1% TiO_2. And that with 0. 8% carbon black is the best.

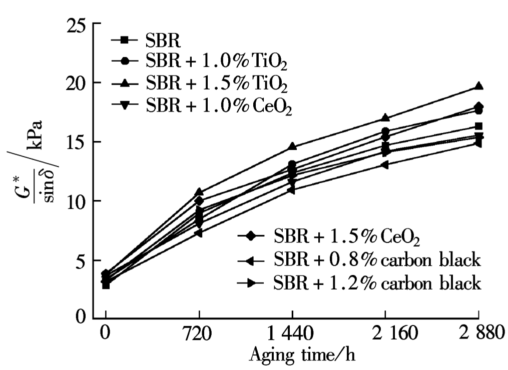

Fig. 5 Relationships between $G^*/\sin\delta$ (58 ℃) of asphalts and aging time

3. 2. 3 Direct tension testing (DTT)

Results of direct tension testing (DTT) are plotted in Fig. 6. In this figure, the 1% tangent modulus of all modified asphalts increases under UV radiation, that is, low-temperature performance decreases. Low-temperature perform-

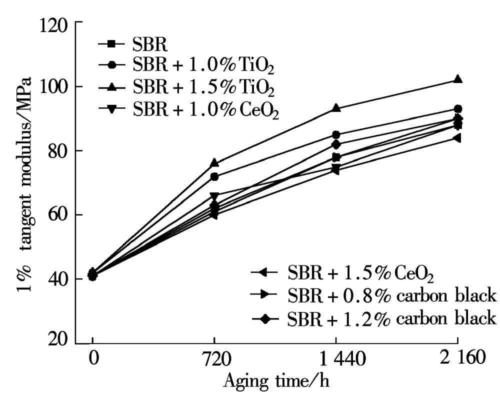

Fig. 6 Relationships between 1% tangent modulus (-10 ℃) of asphalt and aging time

ance of asphalt with carbon black is much better than that with TiO_2. When carbon black content reaches 1.2%, the tangent modulus is a little larger than that of SBR asphalt. These results show that asphalt with excessive carbon black is harmful to low-temperature performance, and should be controlled within 0.8% of asphalt weight.

4 Infrared Absorption Spectral Analysis

Infrared absorption spectral analysis is one of the most commonly used methods for petroleum-asphalt chemical structure analysis. When infrared light with continuous wavelengths (wavenumber 1 600 to 650 cm^{-1}) radiates through a material, transitions of molecular vibration and rotational energy occur as the material absorbs certain wavelengths of light. Changes in light absorbance curves of different wavelengths result in infrared absorption spectra.

4.1 Specimen production

A set of smears are coated with SBR asphalt film with 0.8% carbon black, and other set of smears are coated with SBR asphalt only. After preparation, two sets of specimens are placed into a UV-aging tester. IR analyses are then carried out for UV-aged specimens with 500, 1 000 and 1 500 h aging time, respectively.

4.2 Spectral analysis

During the asphalt aging process, micro-structural changes of asphalt can be shown as the carbonyl peak in the wavenumber 1 695 cm^{-1} of the infrared spectra curve (see Fig. 7). The sharper the curve, the bigger the carbonyl peak index and the more severe the asphalt aging. The carbonyl peak index can be calculated by

$$I = \int_{\lambda_1}^{\lambda_2} \tilde{\omega} d\lambda \tag{1}$$

where λ_1 and λ_2 are the initial and the final wavelengths, respectively; $\tilde{\omega}$ is the average relative strength of the carbonyl absorption band.

For different aging times, transmittance percentages of carbon black modified asphalts are plotted in Fig. 7. It can be determined that, after 500 h aging, the carbonyl peak index of asphalt without carbon black I_{un} is 1 653.7, and the carbonyl peak index with carbon black I_t is 824.5. The latter is only 1/2 of the former.

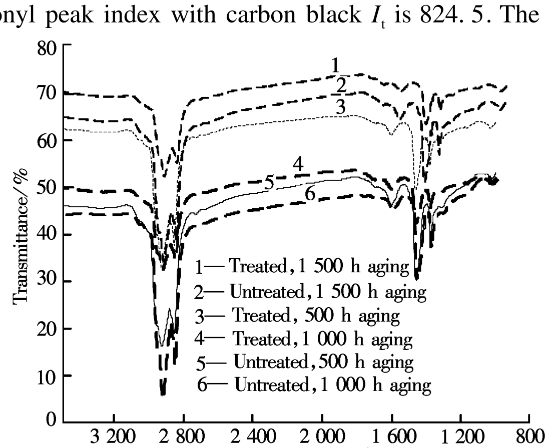

Fig. 7 Infrared absorption spectral analysis of carbon-black-modified asphalt smears

After 1 000 h aging, I_{un} and I_t are 1 877.7 and 1 002.4, respectively. And after 1 500 h aging, I_{un} and I_t are 2 989.3 and 2 346.7, respectively.

It can be seen that UV aging of asphalt mainly occurs in the early stage. The carbonyl peak index of asphalt with/without carbon black increases with aging time. After 1 500 h aging, I_t is still 642.6 smaller than I_{un}. This indicates that carbon black can delay UV aging of asphalt.

5 Determination of Optimal Contents of Three Anti-UV-Aging Agents

Grey incidence analysis is an important component of grey system theory proposed by Deng in 1982[11]. By calculating grey incidence between target values (reference series) and effect factors (compared series), main factors which affect target values can be determined[11]. Therefore, grey incidence analysis can be used to determine optimal contents of the three anti-UV-aging agents.

5.1 Grey incidence analysis of three anti-UV-aging agents

Taking retained penetration after TFOT (2 800 h), Brookfield rotary viscosity and $G^*/\sin\delta$ of aged asphalts as evaluation indices, results of grey incidence analysis are shown in Tab. 3. It can be seen that carbon-black-modified asphalt has the best effect on UV aging, and Nano-TiO_2 modified asphalt worst.

Tab. 3 Grey incidence analysis of three anti-UV-aging agents

Item	Retained penetration	Brookfield rotary viscosity/(Pa·s)	$\frac{G^*}{\sin\delta}$/kPa	Grey incidence
SBR	0.59	1.664	16.321	
SBR + 1.0% TiO_2	0.58	1.983	17.647	0.92
SBR + 1.0% CeO_2	0.79	1.817	15.564	0.96
SBR + 0.8% carbon black	0.65	1.613	14.887	0.99

5.2 Optimal contents of three anti-UV-aging agents

Tab. 4 shows the results of grey incidence analysis of asphalts with different contents of three anti-UV-aging agents after 2 880 h aging. It can be seen that grey incidence of asphalt with 1.0% TiO_2 is the largest and its optimal content is 1.0%; grey incidence of asphalt with 1.0% CeO_2 is the largest and its optimal content is 1.0%; grey incidence of asphalt with 0.8% carbon black is the largest and its optimal content is 0.8%. These are in accord with the above test results.

Tab. 4 Grey incidence analysis of three anti-UV-aging agents with different contents

Item	Retained penetration	Brookfield rotary viscosity/(Pa·s)	$\frac{G^*}{\sin\delta}$/kPa	Grey incidence
SBR	0.59	1.664	16.321	
SBR + 1.0% TiO_2	0.58	1.983	17.647	0.94
SBR + 1.5% TiO_2	0.54	2.231	19.635	0.90
SBR	0.59	1.664	16.321	
SBR + 1.0% CeO_2	0.79	1.817	15.564	0.97
SBR + 1.5% CeO_2	0.74	2.117	17.983	0.92
SBR	0.59	1.664	16.321	
SBR + 0.8% carbon black	0.65	1.613	14.887	1.00
SBR + 1.2% carbon black	0.69	1.911	15.391	0.94

6 Conclusions

With SBR asphalt commonly used in the Tibetan Plateau, this paper investigates indices changes of UV-aged asphalts with three anti-UV-aging agents. Main conclusions can be drawn as follows:

1) TiO_2 and CeO_2 are UV absorbing and shielding agents, and also oxidants. When their contents in asphalt exceed a certain amount, strong oxides produced under UV radiation will accelerate oxidation of asphalt. Oxidation of TiO_2 is stronger than that of CeO_2.

2) For SBR asphalt with 1.0% TiO_2, its incremental rotary viscosity results not only from aging time, but also from TiO_2 itself. Contrarily, for the other two asphalts, their incremental rotary viscosities result mainly from aging time, not from CeO_2 and carbon black.

3) Carbon black is a good UV absorbing and shielding agent. UV absorption is stronger as carbon black content increases. So carbon black is recommended to be used in asphalt pavements in the Tibetan Plateau.

4) Infrared absorption spectral analysis of UV-aged asphalt with 0.8% carbon black shows that carbon black can delay UV aging of asphalt. And UV aging of asphalt mainly occurs in the early stages. The longer the aging time, the more severe the aging of asphalt.

5) Grey incidence analysis of asphalt with TiO_2, CeO_2 and carbon black indicates that carbon black modified asphalt has the best effect on UV aging, and TiO_2 modified asphalt the worst. The optimal content of carbon black is 0.8% asphalt weight.

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适应西藏高原环境的沥青抗紫外线老化试验研究

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摘要:紫外线是导致西藏高原沥青路面早期损害的主要原因之一. 根据实测的紫外线辐射水平,进行了不同掺量的 3 种纳米级抗紫外线老化剂(TiO_2,CeO_2 和炭黑)的 SBR 沥青紫外线老化试验. 针对老化后的沥青,进行了常规指标(TFOT 后的针入度比、软化点)和 SHRP 指标的评价. 针对已老化不同时间(500,1 000 和 1 500 h)的、掺加 0.8% 炭黑的沥青,分别进行了红外光谱分析. 采用灰色关联分析法,确定了抗紫外线老化剂的最佳掺量. 结果表明,TiO_2 和 CeO_2 不仅是好的紫外线吸收或屏蔽剂,而且是一种强氧化剂;炭黑是良好的抗紫外线老化剂,其最佳掺量为沥青质量的 0.8%;沥青紫外线老化主要发生在老化前期,老化时间越长老化越严重.

关键词:紫外线老化;抗老化剂;炭黑;红外光谱分析;灰色关联分析

中图分类号:U214.7⁺5