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[Research Note]

Reinforcing Effects of Carbon Black on Asphalt Binder for Pavement

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Carbon black, used as a reinforcing filler for rubber materials, was evaluated for asphalt binders in pavements. Carbon black added to straight asphalt within 20 wt% caused an increase in the elastic modulus and a decrease in the viscosity of the asphalt, especially at temperatures higher than room temperature. Addition of carbon black raised the maximum service temperature of asphalt in the category of the binder performance grade according to the SHRP (Strategic Highway Research Program) specifications. On the other hand, addition of carbon black also increased the failure strain at low temperatures. Furthermore, addition of carbon black reduced the coefficient of thermal expansion (CTE) of asphalt to closer to that of aggregates. In asphalt mixtures, tensile stress occurs at the boundary between asphalt and aggregate with decreasing temperature due to the CTE difference. Addition of carbon black reduced this stress. Carbon black addition to asphalt has the potential to improve both deformation resistance in the high temperature region and crack resistance in the low temperature region, which were empirically considered to be contradictory. Therefore, carbon black is an effective filler for improving the durability of asphalt pavements.

Keywords
Asphalt binder, Reinforcement, Carbon black, SHRP

1. Introduction

Asphalt pavements are constructed depending on the thermo-plasticity of asphalt, which is the property of softening by heating and hardening by cooling. However, these effective properties become disadvantages for in-service periods, as rutting of pavements occurs in a hot summer and cracking in a cold winter. These phenomena are the main modes of failure of asphalt pavements. Experience has shown that harder asphalts tend to resist rutting but are more sensitive to cracking, and *vice versa*. The use of hard asphalts modified with resins and/or thermoplastic elastomers has recently become commonplace as a countermeasure for improving rutting resistance. However, longitudinal surface cracking tends to occur more easily with a modified asphalt Type Ⅱ binder than with a straight asphalt binder[1)]. Degradation of polymeric modifiers also occurs during service[2)].

We previously confirmed that carbon black[3)], used as a reinforcing filler for rubber materials, helps to prevent photodegradation by ultraviolet irradiation[4),5)]. Carbon black is a solid material that is heat and light stable, so does not undergo change and therefore has potential as a reinforcing filler for improving the durability of asphalt materials. Previous experimental addition of carbon black to asphalts has focused on properties such as viscosity and/or penetration in the high temperature region by conventional test methods[6)~9)]. There are no reports on the detailed study of viscoelasticity in the cold temperature region by using the SHRP (Strategic Highway Research Program) test methods[10)], which is being recognized in the paving industry. The present study investigated the properties of straight asphalt with carbon black content of up to 20 wt% (pha = parts per hundred asphalt by weight) over a wide temperature range to assess the potential of carbon black to improve both deformation resistance in the high temperature region and crack resistance in the low temperature region.

2. Experiment

2. 1. Materials

The base asphalt binder used in the experiment was commercially available straight asphalt (StAs) with the basic properties listed in **Table 1**. The carbon black was #7350F (Tokai Carbon Co., Ltd.) with the basic properties shown in **Table 2**. StAs with carbon black

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Table 1 Properties of Asphalt Binder

Test item		StAs	Test specification
Penetration at 25°C	[1/10 mm]	90	JIS K 2207-6.3
Softening point	[°C]	46.0	JIS K 2207-6.4 R&B
Viscosity at 135°C	[mPa·s]	365	JIS K 2207-6.14 Cannon-Fenske
Density at 15°C	[g/cm^3]	1.033	JIS K 2207-6.12 Hubbard bottle
Flash point	[°C]	348	JIS K 2265-7 COC

Table 2 Properties of Carbon Black

Test item		CB	Test specification
Surface area by N_2 adsorption	[m^2/g]	80	JIS K 6217-7 BET
DBP absorption[a)]	[cm^3/100 g]	100	JIS K 6217-9
Aggregate size Dst[b)]	[nm]	90	ASTM D 3849 DCF

a) Void volume of bulk carbon black using dibutylphthalate as absorbent.
b) Equivalent Stokes' diameter measured by disc centrifuge (DCF).

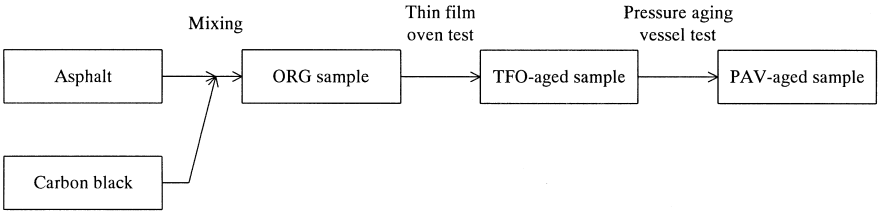


Fig. 1 Test Procedures for Sample Preparation

content of 10 and 20 pha are expressed as CB10 and CB20, respectively.

2. 2. Methods of Sample Preparation

Asphalt binder samples were prepared through the procedure shown in **Fig. 1**. Carbon black was predried at 150°C for 24 h and then kneaded with StAs for 45 min in a mixer (Dalton, universal mixer 2XDMV-Qr) with a bath temperature of 60°C. Kneading at high viscosity provided high shear force and uniform dispersion of carbon black in the asphalt without lump formation. Unaged samples at this step were named original samples (ORG). Subsequently, the thin-film oven test (TFO test)[11),12)] and then the pressure aging vessel test (PAV test, SHRP-B005)[10)] developed by SHRP were performed as indoor accelerated aging tests. Samples from these tests were named TFO-aged and PAV-aged, respectively.

2. 2. 1. TFO Test

Unaged ORG samples were processed by the TFO test based on JIS K 2207[11)], in which 50±0.5 g asphalt samples poured into the designated 140-mm diameter plate were exposed in air for 5 h at 163°C. The TFO test is supposed to simulate short-term aging such as volatilization of light components and/or thermal degradation during mixing in plants and paving construction.

2. 2. 2. PAV Test

TFO-aged samples were subsequently processed by the PAV test based on SHRP-B005[10)], in which the 140-mm diameter plate after TFO testing was placed in air under 2.1±0.1 MPa for 20 h at 100°C. This test is designed to simulate the long-term aging of asphalt that occurs in the pavement after 5 to 10 years of service.

2. 3. Test Items

2. 3. 1. Dynamic Shear Rheometer Test

Dynamic viscoelastic properties of asphalt binders in the temperature region higher than room temperature were examined according to the SHRP-B003 method[10)] using a dynamic shear rheometer (DSR, Rheometrics Co., Ltd.). Dynamic modulus and loss tangent (tanδ) were obtained by measuring the torque with a constant frequency vibration in the direction of rotation applied to the asphalt sample sandwiched between a pair of parallel circular plates. According to the SHRP specifications, the $|G^*|/\sin\delta$ is an indicator of permanent deformation, and the loss modulus, G'' ($=|G^*|\sin\delta$), is an indicator of fatigue cracking, where G^* is called the dynamic complex modulus and δ is the phase angle between stress and strain. Measurements were performed at 10 rad/s using 8-mm diameter parallel plates with a gap of 2 mm in the range of 0 to 40°C, and 25-mm diameter parallel plates with a gap of 1 mm in the range of 50 to 70°C.

2. 3. 2. Bending Beam Rheometer Test

Static viscoelastic properties of asphalt in the lower temperature region below 0°C were examined accord-

ing to the SHRP-B002 method[10] using a bending beam rheometer (BBR, Cannon Instruments Co., Ltd.). This is a type of three-point bending creep test, in which a constant load of 0.98 N is applied to a molded beam specimen immersed in a cooling medium at a constant temperature. According to the SHRP specifications, this test is supposed to be performed at the minimum service temperature plus 10°C. The stiffness, which is obtained from the deformation after loading of 60 s, is an indicator of stress caused by thermal contraction. The *m*-value, which is defined as the slope of the stiffness *versus* time curve plotted on double logarithmic coordinates at the loading time of 60 s, is an indicator of stress relaxation ability. In this study, PAV-aged samples were molded as beam specimens 12.5 mm wide by 6 mm high by 125 mm long, and measured in ethanol medium in the range of −20 to −5°C at 5°C intervals.

2. 3. 3. Destructive Bending Test

The destructive bending test was performed to evaluate the failure properties of asphalt under low temperature. Failure strain calculated by Eq. (1)[13] was selected as an indicator of crack resistance. A beam specimen 20 mm wide by 20 mm high by 120 mm long was used for the test. The span length was 80 mm and the loading rate was 100 mm/min. These conditions are based on the test specifications of the Japan Modified Asphalt Association[13]. Measurements should be performed at −20°C in the standard specification for which the major target is unaged samples of high-viscosity modified asphalt. However, in this study, the test temperature was set at −5°C, because the study target was PAV-aged straight asphalt, which represents the condition of long-term aging. Measurements in this study were performed at around the transition point (the turning temperature from the stress relaxation region to the elastic region), which depends on the strain rate[14].

$$\varepsilon = \frac{6h}{L^2} \cdot d \qquad (1)$$

ε: failure strain
h: thickness of specimen (20 mm)
L: span length (80 mm)
d: deformation at failure (mm)

2. 3. 4. Density Measurement and Calculation of the Coefficient of Thermal Expansion

The coefficients of thermal expansion of asphalt were calculated as follows. First, density was measured by the Hubbard bottle method. The TFO-aged sample, which represents the aging condition soon after paving, was used to investigate the properties of asphalt in asphalt mixtures. Besides the measurement at 15°C based on the specifications of JIS K 2207[11], additional measurements at 5, 25 and 50°C were also performed. The relationship between the inverse of the measured density, *i.e.* specific volume, and test temperatures was linearly approximated by the least-squares method. The coefficient of linear thermal expansion (CTE) was calculated by substituting the slope, *i.e.* the coefficient of cubic expansion, in Eq. (2).

$$\mathrm{CTE} = \left[\left(\frac{\mathrm{d}(1/\rho)}{\mathrm{d}T}\right)+1\right]^{1/3} - 1 \qquad (2)$$

ρ: density (g/m^3)
T: temperature (°C)

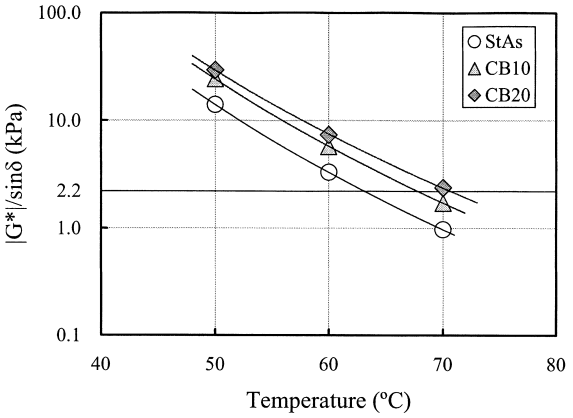


Fig. 2 $|G^*|/\sin\delta$ of TFO-aged Samples with and without Carbon Black by DSR

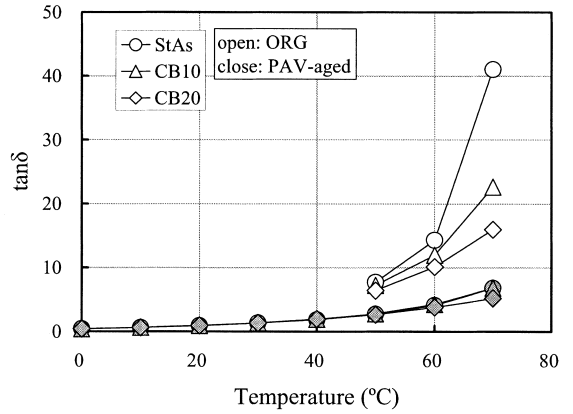


Fig. 3 tanδ of ORG and PAV-aged Samples with and without Carbon Black by DSR

3. Results

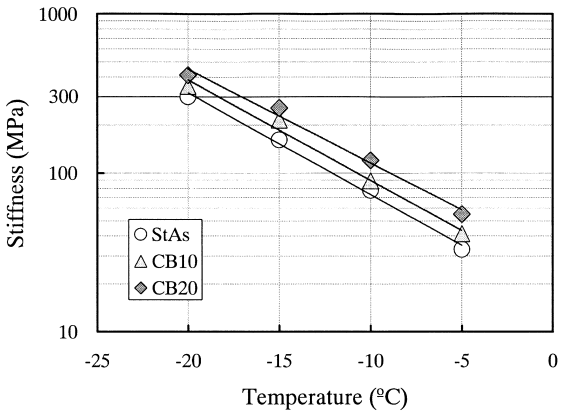
3. 1. Viscoelastic Properties

Figure 2 shows the relationship between test temperature and $|G^*|/\sin\delta$ of TFO-aged samples measured by the DSR test. **Figure 3** shows the relationship between test temperature and tanδ of ORG and PAV-aged samples. As the carbon black content increased, $|G^*|/\sin\delta$ increased and tanδ decreased. Although the effects of carbon black addition were found in ORG, TFO-aged, and PAV-aged samples, the trends were

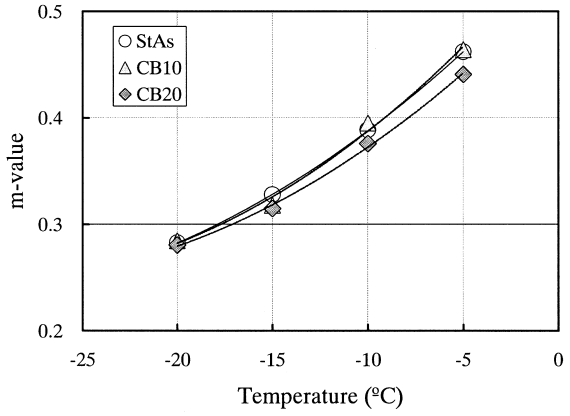
more obvious in the higher temperature region of the ORG samples.

Figures 4a) and **4b)** show the relationships between stiffness and test temperature, and *m*-value and test temperature, respectively, measured by the BBR test. The stiffness was increased by adding carbon black. On the other hand, the *m*-values of StAs and CB10 were very similar, and those of CB20 were slightly smaller.

The results of the DSR test and the BBR test were checked against the performance grade (PG) of the SHRP specifications as shown in **Table 3** and **Fig. 5**. The StAs used in this study was classified as $PG_{58\text{-}22}$. The performance was equivalent to commercially available straight asphalts with a penetration grade of 80/100[15], which are also plotted in **Fig. 5**. On the other hand, carbon-black-containing asphalts, CB10 and CB20, changed in classification to $PG_{64\text{-}22}$ and to $PG_{70\text{-}22}$, respectively, indicating that the service temperature range was expanded to higher temperatures without deterioration of the properties in the low temperature region.



a) Stiffness



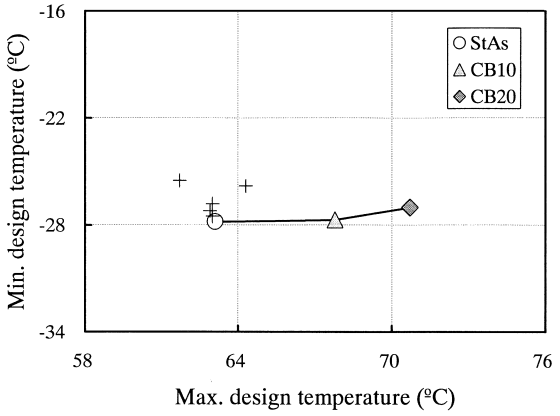
b) m-value

Fig. 4 Stiffness and *m*-value of PAV-aged Samples with and without Carbon Black by BBR

3. 2. Failure Properties and CTE

Figure 6 shows the results of the destructive bending test. The failure strain of the PAV-aged sample increased monotonically with increasing carbon black content. In particular, the failure strain of CB20 was almost two times larger than that of StAs. This suggests that carbon black has the potential to improve failure properties such as cracking.

Figure 7 shows the CTE calculated from the measured density of TFO-aged samples with and without carbon black in the range of 5 to 50°C. The CTE of StAs was about 190×10^{-6}/°C. CTE tended to decrease monotonically with increasing carbon black content up to 20 pha. Incidentally, CTEs of CB10 and



+: commercially available StAs80/100[15].

Fig. 5 Changes in PG Caused by Adding Carbon Black

Table 3 PG-binder Grading System According to the SHRP

Sample	Test method	Specification	Temperature [°C]		
			StAs	CB10	CB20
ORG	DSR	$\lvert G^* \rvert / \sin\delta \geq 1.0$ kPa	65.2	68.6	72.9
TFO-aged	DSR	$\lvert G^* \rvert / \sin\delta \geq 2.2$ kPa	63.1	67.8	70.7
PAV-aged	DSR	$\lvert G^* \rvert \sin\delta \leq 5.0$ MPa	19.9	21.8	22.7
	BBR	Stiffness ≤ 300 MPa	−19.6	−18.3	−17.0
		m-value ≥ 0.3	−17.8	−17.7	−17.0
PG			$PG_{58\text{-}22}$	$PG_{64\text{-}22}$	$PG_{70\text{-}22}$

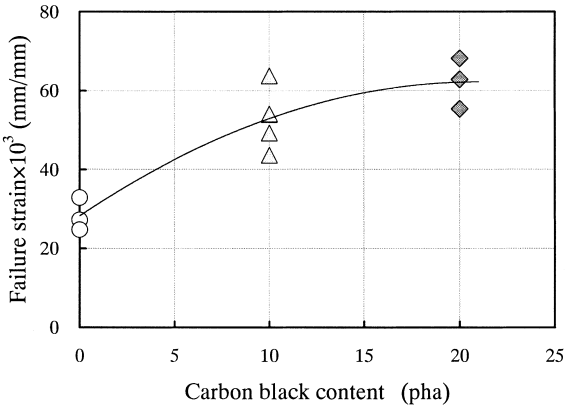


Fig. 6 Effects of Carbon Black on the Failure Strain of PAV-aged Samples by Destructive Bending Test

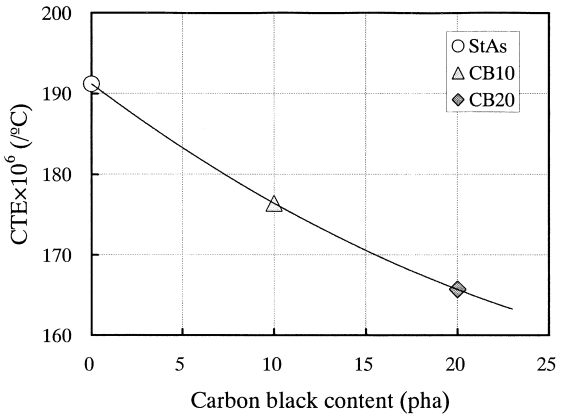


Fig. 7 CTE of TFO-aged Sample with and without Carbon Black

CB20 were reduced by about 8% and 13%, respectively, compared to StAs.

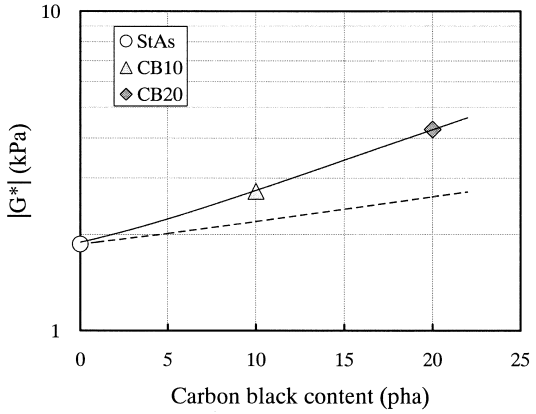
4. Discussion

4. 1. Improvement of Deformation Resistance by Adding Carbon Black

Addition of carbon black to StAs increased $|G^*|/\sin\delta$ (**Fig. 2**) and decreased $\tan\delta$ (**Fig. 3**), especially in the region higher than 50°C. This phenomenon is discussed below with reference to the reinforcing mechanism of carbon black in rubber materials, in which carbon black is the most important reinforcing filler. **Figure 8** shows the relationship between carbon black content and $|G^*|$ at 60°C in the ORG sample. The curve calculated by Guth–Gold's equation (Eq. (3)[3),16)]), which is commonly used in the reinforcement theory of the particle dispersion system based on hydrodynamic interaction, is also plotted in **Fig. 8**.

$$|G^*| = |G^*_{StAs}| (1 + 2.5\phi + 14.1\phi^2) \quad (3)$$

G^*_{StAs}: Dynamic complex modulus of StAs without carbon black



------: Guth–Gold's equation (Eq. (3)).

Fig. 8 Changes of $|G^*|$ at 60°C Caused by Adding Carbon Black

G^* : Dynamic complex modulus of asphalt with carbon black of a volume fraction, ϕ

As the volume fraction (ϕ) of carbon black is increased, the measured values of the $|G^*|$ tended to deviate from the curve calculated by Eq. (3). Rubber materials show a similar tendency. A component called carbon gel or bound-rubber, which is insoluble in organic solvents such as toluene, generated at the boundary between carbon black and rubber is believed to be closely involved in this effect. This interpretation is based on the concept that formation of an insoluble component or network around the carbon black particles acts as the effective reinforcing volume. However, our experiments did not detect any insoluble component in the composite system of asphalt and carbon black.

A possible explanation for the observed behavior of carbon black-containing asphalt is as follows. Although Eq. (3) is a function of only ϕ, the effects of absorption on the surface will become larger as the particle size is reduced. On the other hand, the properties of the asphalt film binding porous aggregates are different from those of bulk asphalt because the light components of asphalt such as saturates and aromatics are preferentially absorbed into the pores of the aggregates[17),18)]. Since carbon black can easily absorb low molecular weight components due to its lipophilic (or hydrophobic) nature and large specific surface area of about 100 m^2/g, addition of carbon black to the asphalt is likely to increase the elastic modulus. Furthermore, from the aspect of the binder PG based on the SHRP specifications, addition of carbon black raises the maximum service temperature, resulting in improved rutting resistance of asphalt pavements in the high temperature region.

4. 2. Improvement of Crack Resistance by Adding Carbon Black

The improvement in the viscoelastic properties due to carbon black addition seem to occur in the high temperature region without changing the asphalt properties in the low temperature region. However, we found that the CTE of asphalt was decreased by adding carbon black (**Fig. 7**) and the failure strain in the destructive bending test was increased in the lower temperature region below 0°C (**Fig. 6**). The effects of these changes in asphalt properties, caused by adding carbon black, are considered on the performance of asphalt pavements at low temperatures.

Transverse cracking, referred to as low temperature cracking, is caused by contraction of the asphalt pavement with decreasing outdoor air temperature, and is a serious problem in cold regions. Low temperature cracking may occur when the stress resulting from the difference of the CTE at the boundary between asphalt and aggregate exceeds the critical strength of the asphalt pavements, because the CTE (about 2 to 5×10^{-6}/°C) of aggregate is much smaller than that of asphalt[19]. According to the present study, carbon black addition reduces the CTE of asphalt. Therefore, the stress produced at the boundary between asphalt and aggregate will diminish. Addition of solid paraffin to asphalt increases the specific volume change with temperature[20]. Conversely, absorption of light components such as paraffin by carbon black might reduce CTE. Another possibility is that the effect of steric hindrance by the three-dimensional network of carbon black prevents deformation (expansion and/or contraction).

The increase in failure strain caused by adding carbon black (**Fig. 6**) might result from disrupting the state of stress and/or strain in the asphalt matrix, and consequently distributing the applied load over the entire system. The failure strain of asphalt binder is a determining factor of low temperature cracking[21]. Carbon black addition is supposed to be much more effective against low temperature cracking because of the increased failure strain in addition to the reduction of CTE. Solid paraffin-containing asphalt tends to be destroyed by a slight impact[20]. On the contrary, absorption of light components by carbon black may have caused the increase of critical strain in this study. In a previous paper[5], we confirmed that the saturates among the chemical fractions of asphalt were the most sensitive to light (ultraviolet irradiation), and carbon black addition prevented photodegradation. Therefore, preferential absorption of light components by carbon black will contribute to the effective control of photodegradation.

5. Conclusions

Carbon black, used as a reinforcing filler for rubber materials, was added to asphalt binder for pavements. Properties of the straight asphalt with carbon black content up to 20 wt% (pha = parts per hundred asphalt) were as follows.

Addition of carbon black to asphalt increased the elastic modulus and decreased the viscosity, especially in the temperature region higher than room temperature. Carbon black raised the maximum service temperature in the category of the binder PG according to the SHRP specifications. On the other hand, carbon black addition increased the failure strain of asphalt at low temperatures. Furthermore, carbon black reduced the CTE of asphalt. Reduced CTE difference between asphalt and aggregate indicates that the stress derived at the boundary with decreasing temperature in asphalt mixtures will be reduced.

Carbon black addition to asphalt can improve the deformation resistance in the high temperature region and the crack resistance in the low temperature region. Therefore, carbon black is an effective filler for improving the durability of asphalt pavements.

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要　　旨

カーボンブラック添加による舗装用アスファルトの補強効果

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ゴム材料の補強用充填材として知られるカーボンブラックを取り上げ，舗装用アスファルトへの利用の可能性について検討を行った。20 wt％（外割，pha＝parts per hundred asphalt）までの範囲でカーボンブラックを添加したストレートアスファルトの性状を調べた。

常温域から高温側において，カーボンブラックの添加はアスファルト単体の弾性率を増大させ粘性傾向を低下させた。これにより，SHRP（Strategic highway research program）規格のパフォーマンスグレードの分類上，供用可能な温度範囲が高温側に拡大することが確認された。一方，低温域ではカーボンブラックの添加は破壊時のひずみを大きくすることが判明した。さらに，カーボンブラック添加は，アスファルトの熱膨張係数を小さくし，骨材のそれに近づける効果も生み出した。アスファルト混合物では，温度の低下に伴いアスファルトと骨材の熱膨張係数の差に起因してその界面に応力が発生することが知られているが，カーボンブラックの添加はこの応力の軽減にも貢献することが期待される。

アスファルトへのカーボンブラックの添加は，経験的に相反する性状とされている高温域における変形に対する抵抗性と低温域におけるひび割れに対する抵抗性を両立して改善できる可能性があり，アスファルト舗装の耐久性を向上する一つの有効な策と考えられる。