

# Effects of carbon black on the thermal, mechanical and electrical properties of pitch-matrix composites

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## Abstract

The softening temperature of asphalt (pitch-matrix composite containing sand) was increased from 44 to 81 °C upon addition of 7.0 vol.% carbon black. Accompanying effects are increase of the storage modulus, decrease of the damping capacity and decrease of the electrical resistivity. All these effects increase with increasing carbon black content. Carbon black and sand together are much more effective than carbon black alone or sand alone for raising the softening temperature. Carbon black is more effective than silica fume for raising the softening temperature, but is less effective for increasing the storage modulus.

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## 1. Introduction

Asphalt is a widely used construction material. It is most commonly used for road pavement [1] and roofing [2–5]. Asphalt is a pitch-matrix composite containing aggregates such as sand and gravel. One of the shortcomings of asphalt is its low softening temperature—a consequence of the low softening temperature of the pitch-matrix. The low softening temperature of asphalt limits the application of this material to structures that do not encounter temperatures exceeding 40 °C. In addition, it limits the performance and durability of asphalt. Rutting is a particularly common durability problem for asphalt road pavements in warm climate areas [6].

The addition of polymers (e.g., latex) and carbon blacks is used to improve the mechanical and rheological properties of asphalt [7,8]. In particular, the addition of carbon black is effective for reducing the rutting potential in warm climate areas [7]. This effect of carbon black relates to the increase of the stiffness, especially at high temperatures [8,9].

Prior work has shown that the addition of silica fume (SiO<sub>2</sub> particles of typical size around 0.1 μm) to asphalt

increases the softening temperature from 44 to 50 °C [10]. The silica fume amounts to 1.9 vol.% of the asphalt (equivalent to 5.0% by weight of pitch [10]). Increasing the silica fume content from 1.9 to 5.4 vol.% causes the softening temperature of the asphalt to increase from 50 to just 51 °C, but causes the flexural storage modulus at 0.2 Hz to decrease from 3.6 to 0.5 GPa [10]. Thus, a high silica fume content of 5.4 vol.% is undesirable.

The silica fume increases the softening temperature, presumably because its small particle size results in a large area of the interface between silica fume and the pitch-matrix per unit volume of the composite and the pitch at or near the interface is restrained from softening. Based on this notion and prior work of carbon black in asphalt [7,8] and pitch [11], this paper uses carbon black instead of silica fume. Carbon black is in the form of a porous agglomerate of nanoparticles (30 nm in size for the carbon black used in this work). This microstructure results in a relatively large surface area per unit volume. Furthermore, carbon black is known to be wetted well by organic liquids [12]. Therefore, in spite of the low stiffness of carbon black compared to silica fume, carbon black is expected to be attractive for use in pitch. Indeed, this work has shown that carbon black is highly effective in raising the softening temperature of asphalt. By using 7 vol.% carbon black in asphalt, the softening temperature of asphalt is increased from 44 to 81 °C.

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In addition to investigating the softening temperature, this paper evaluates the dynamic flexural properties, due to the relevance of flexural properties to the structural use of asphalt. The flexural properties were studied at low loading frequencies due to the low frequencies encountered by large structures. The flexural properties measured were the storage modulus and the loss tangent. The storage modulus reflects the stiffness, whereas the loss tangent ( $\tan \delta$ ) is the damping capacity. Both high stiffness and high loss tangent are desirable for structural applications.

Due to the electrical conductivity of carbon black and the non-conductive nature of pitch or sand, the addition of carbon black to pitch or asphalt is expected to decrease the electrical resistivity, especially when the carbon black volume fraction exceeds the percolation threshold. For the purpose of obtaining information on the extent of contact among carbon black particles in the pitch-matrix composite, this paper includes measurement of the DC electrical resistivity.

This paper is aimed at studying the effects of carbon black addition on the thermal, mechanical and electrical properties of pitch-matrix composites. The effects were studied in both the presence and absence of sand. Sand is very different from carbon black in its particle size and stiffness. Study of the separate and combined effects of carbon black and sand is expected to shed light on the origin of the property changes.

## 2. Experimental methods

The pitch used was 170 Petroleum Pitch from Crowley Tar Products Company, Inc. (New York, NY). Its density was  $1.21 \text{ g/cm}^3$ . The aggregate used was natural sand of density  $2.88 \text{ g/cm}^3$  (as measured by using the Archimedes' Principle). The particle size analysis of the sand (all passing #25 US sieve, 0.710 mm aperture 99.9%  $\text{SiO}_2$ ) is shown in Fig. 1 of Ref. [13]. The sand/pitch ratio was 1.0.

The carbon black was Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. This carbon black was chosen due to its electrical conductivity and easy dispersion. It was in the form of porous agglomerates of carbon particles of average size 30 nm, a nitrogen specific surface area of  $254 \text{ m}^2/\text{g}$ , a volatile content of 1.07%, a maximum ash content of 0.2% and a density of  $1.7\text{--}1.9 \text{ g/cm}^3$ .

Pitch was first melted in a steel container by using a hot plate at  $120 \text{ }^\circ\text{C}$  and mixed in the molten state by hand for 10 min with a chosen amount (1.9, 5.4 or 7.0 vol.% of the pitch) of carbon black. Sand, if applicable, was added to the mix. The mixture was allowed to cool to room temperature. After solidification, the pitch-based material was ground by hand into composite particles of size around 0.1–1 mm. These particles were

placed in a  $160 \times 15 \text{ mm}$  steel mold cavity and then melted at  $120 \text{ }^\circ\text{C}$  for 15 min by using a hot plate. Immediately after melting, a matching steel piston was placed in the mold cavity. The pressure, as provided by a combination of piston weight and manual force, ranged from 0.09 to 0.36 MPa. The higher the carbon black content, the greater was the pressure used. Subsequent cooling and demolding resulted in specimens of size  $160 \times 15 \times 3.5 \text{ mm}$ . In the case of pitch without carbon black, the procedure was the same except that the pitch particles placed in the mold were obtained by crushing the solid pitch without prior melting.

The mechanical properties under flexure were studied by dynamic mechanical testing at controlled frequencies (0.2, 1.0 and 2.0 Hz) and room temperature ( $20 \text{ }^\circ\text{C}$ ), using a Perkin-Elmer Corp. (Norwalk, CT) Model DMA 7E dynamic mechanical analyzer. Measurements of storage modulus were made at various constant frequencies. The specimens were in the form of beams ( $160 \times 15 \times 3.5 \text{ mm}$ ) under three-point bending, such that the span was 150 mm. The loads used were all large enough so that the amplitude of the specimen deflection was from 6.0 to  $9.0 \text{ }\mu\text{m}$  (over the minimum value of  $5 \text{ }\mu\text{m}$  required by the equipment for accurate results). The loads were set so that each different type of specimen was always tested at its appropriate stress level. Six specimens of each type were tested.

The softening temperature was measured by performing thermal mechanical analysis (TMA) in the penetration mode at a compressive stress of 1415 Pa (as applied through a quartz probe with a flat tip of diameter 3 mm), using a Perkin-Elmer Corp. (Norwalk, CT) Model TMA 7E thermal mechanical analyzer. The heating rate was  $2 \text{ }^\circ\text{C}/\text{min}$ . The sample size was  $8 \times 5 \text{ mm}$  in the plane perpendicular to the stress direction and 3.5 mm in the stress direction, as obtained by cutting the specimens described above. The softening temperature was taken as the intersection of the extrapolation of the baseline with the tangent of the TMA curve (i.e., curve of the fractional change in dimension in the stress direction vs. temperature) in the high temperature regime.

The electrical resistivity was measured on specimens of size  $160 \times 15 \times 3.5 \text{ mm}$ . The four-probe method was used for specimens of resistivity around  $10^5 \text{ }\Omega\text{cm}$  or less; the two-probe method was used for specimens of resistivity above  $10^6 \text{ }\Omega\text{cm}$ . In the four-probe method, the outer two electrical contacts are for passing current; the inner two electrical contacts are for measuring the voltage. In the two-probe method, two contacts were used such that each contact was for both current and voltage. Silver paint in conjunction with copper wire was used for the electrical contact. Each electrical contact was around the entire perimeter of the specimen in a plane perpendicular to the length of the specimen.

### 3. Results and discussion

Table 1 shows the flexural storage modulus of pitch and pitch-matrix composites. At any frequency, the storage modulus was increased by the addition of carbon black to the pitch, while the loss tangent ( $\tan \delta$ ) was decreased. The increase in storage modulus is consistent with prior report of the increase in stiffness [8,9]. At a fixed volume fraction (7%) of carbon black, addition of sand caused the storage modulus to increase and the loss tangent to decrease, as shown by comparing the bottom two entries in Table 1. The increase in storage modulus is consistent with that reported for the addition of silica fume [10]. The loss modulus (the product of the storage modulus and the loss tangent) was not much affected by carbon black addition, due to the opposing effects on the storage modulus and loss tangent.

Prior report [10] on the storage modulus had been made on pitch with sand (without carbon black; same sand and sand content as this work; same testing method as this work), as shown in Table 1. The addition of carbon black to asphalt increased the storage modulus substantially, as shown by comparing the last two rows in Table 1. Consistent with this result is the fact that the storage modulus was increased substantially upon the addition of sand at a fixed carbon black content of 7 vol.%, as shown by comparing the last row and the third last row in Table 1. On the other hand, the loss tangent was decreased by the addition of sand at a fixed carbon black content of 7 vol.%, as shown in Table 1. As a result of the decrease in loss tangent, the loss modulus was reduced.

That the loss tangent (damping capacity) was decreased by the addition of either carbon black or sand is due to the high damping capacity of pitch compared to that of carbon or sand. The high damping capacity of pitch is expected from the polymeric nature of pitch. That the storage modulus was increased by the addition

of either carbon black or sand is due to the reinforcing ability of carbon black and sand.

Fig. 1 shows the TMA result (i.e., fractional change in dimension vs. temperature during heating). Based on Fig. 1, Table 2 was obtained.

Table 2 shows that the softening temperature was increased by the addition of carbon black to pitch. The higher the carbon black content, the higher was the softening temperature. However, in the absence of sand, the softening temperature was increased from 40.1 to 55.6 °C only, even with the highest carbon black content of 7.0 vol.%. On the other hand, the addition of sand greatly increased the softening temperature, as shown by comparing the last entry and the third last entry in Table 2.

Prior work [10] on pitch with sand (without carbon black; same sand and sand content as this work; same pitch as this work; same testing method as this work) showed that the softening temperature is 44.2 °C. Thus the addition of carbon black to asphalt (i.e., pitch with sand) increased the softening temperature from 44.2 to 80.9 °C.

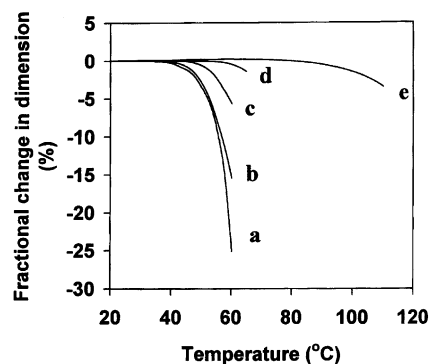


Fig. 1. Fractional change in dimension vs. temperature during heating of (a) pitch without any additive, (b) pitch with 1.9 vol.% carbon black, (c) pitch with 5.4 vol.% carbon black, (d) pitch with 7.0 vol.% carbon black and (e) asphalt with 7.0 vol.% carbon black.

Table 1

Tangent  $\delta$ , storage modulus and loss modulus of pitch-matrix composites with different contents of carbon black and at different loading frequencies

Carbon black content (vol.%)	Frequency								
	0.2 Hz			1.0 Hz			2.0 Hz		
	Tan $\delta$	Storage modulus (GPa)	Loss modulus (GPa)	Tan $\delta$	Storage modulus (GPa)	Loss modulus (GPa)	Tan $\delta$	Storage modulus (GPa)	Loss modulus (GPa)
0 <sup>a</sup>	0.145	0.815	0.120	0.152	1.33	0.205	0.154	1.42	0.220
1.9 <sup>a</sup>	0.124	0.975	0.123	0.118	1.58	0.189	0.114	1.67	0.170
5.4 <sup>a</sup>	0.122	1.13	0.140	0.114	1.86	0.207	0.105	1.96	0.206
7.0 <sup>a</sup>	0.081	1.76	0.146	0.073	3.04	0.219	0.068	3.37	0.227
0 <sup>b,c</sup>	/	1.3	/	/	1.6	/	/	1.8	/
7.0 <sup>b</sup>	0.054	2.09	0.115	0.048	3.53	0.174	0.034	3.61	0.126

<sup>a</sup> Without sand.

<sup>b</sup> With sand.

<sup>c</sup> From Ref. [10].

Table 2  
Softening temperature of pitch-matrix composites with various volume fractions of carbon black, with and without sand

Carbon black content (vol.%)	Softening temperature (°C)
0 <sup>a</sup>	40.1
1.9 <sup>a</sup>	43.0
5.4 <sup>a</sup>	44.9
7.0 <sup>a</sup>	55.6
0 <sup>b,c</sup>	44.2
7.0 <sup>b</sup>	80.9

<sup>a</sup> Without sand.

<sup>b</sup> With sand.

<sup>c</sup> From Ref. [10].

Prior work [10] showed that the softening temperature is increased from 40.9 to 44.2 °C when sand is added to pitch. Thus, the effect of the addition of sand alone on the softening temperature is rather small. As mentioned above, the effect of the addition of carbon black alone on the softening temperature is not large (from 40.1 to 55.6 °C). However, the addition of both sand and carbon black resulted in a much larger effect, so that the softening temperature was raised from 40.1 to 80.9 °C (Table 2). This means that sand and carbon black have synergistic effects, presumably because of the stiffness and low thermal expansion of sand, and the high surface area of carbon black.

Table 3 shows that the volume electrical resistivity decreased from a value that was too high to be measured to  $10^5 \Omega\text{cm}$  upon increasing the carbon black content from 5.4 to 7.0 vol.%, probably because of the attainment of percolation at 7.0 vol.%. Further increase of the carbon black content to 8.6 vol.% caused the resistivity to increase slightly, presumably because of the high porosity resulting from the insufficient proportion of pitch in the composite with 8.6 vol.% carbon black. Addition of sand caused the resistivity to increase from  $10^5$  to  $10^8 \Omega\text{cm}$ , as shown for a fixed carbon black content of 7.0 vol.%. Table 3 also shows that the addition of carbon black to asphalt (with sand) decreased the resistivity from a value which was too high to be measured to  $10^8 \Omega\text{cm}$ .

Table 3  
Electrical resistivity of pitch-matrix composites with various volume fractions of carbon black, with and without sand

Carbon black content (vol.%)	Electrical resistivity ( $\Omega\text{cm}$ )
1.9 <sup>a</sup>	— <sup>b</sup>
5.4 <sup>a</sup>	— <sup>b</sup>
7.0 <sup>a</sup>	$2.76 \times 10^{5c}$
7.0 <sup>d</sup>	$1.0 \times 10^{8e}$
8.6 <sup>a</sup>	$2.9 \times 10^{8e}$

<sup>a</sup> Without sand.

<sup>b</sup> Too high to be measured.

<sup>c</sup> Four-probe method.

<sup>d</sup> With sand.

<sup>e</sup> Two-probe method (valid for measurement of high resistances).

The large drop in resistivity as the carbon black content was increased from 5.4 to 7.0 vol.% (Table 3) is consistent with the relatively large drop in the softening temperature from 45 to 56 °C (Table 2) and with the relatively large increase in storage modulus and the relatively large decrease in loss tangent (Table 1) as the carbon black content was increased from 5.4 to 7.0 vol.%.

From the viewpoint of asphalt technology, the main finding of this paper is the increase in softening temperature of asphalt from 44 to 81 °C upon addition of 7.0 vol.% carbon black. This finding suggests a similar effect of carbon black when sand is replaced by other ceramic particles, which may be used in the fabrication of carbon-matrix composites.

In the presence of sand, carbon black (7.0 vol.%) addition resulted in a softening temperature of 81 °C, whereas silica fume (5.4 vol.%) addition attained 51 °C [10]. Thus, carbon black is more effective than silica fume, though the difference in volume fraction makes the comparison not totally fair. Nevertheless, the highest softening temperature attained by using carbon black (81 °C) is much higher than that attained by using silica fume (51 °C). On the other hand, carbon black is less effective than silica fume for increasing the storage modulus. A storage modulus (0.2 Hz) of 3.6 GPa was attained with silica fume (1.9 vol.%) addition [10], whereas a value of 2.1 GPa was attained with carbon black (7.0 vol.%) addition.

#### 4. Conclusion

Addition of 7.0 vol.% carbon black to asphalt (with sand) resulted in increase of the softening temperature from 44 to 81 °C, increase of the storage modulus (under flexure at 0.2 Hz) from 1.3 to 2.1 GPa, and decrease of the electrical resistivity to  $10^8 \Omega\text{cm}$ . In addition, carbon black addition decreased the loss tangent. All these effects increased with increasing carbon black content. The percolation threshold was probably between 5.4 and 7.0 vol.% carbon black in pitch (without sand). The addition of both carbon black and sand to pitch was much more effective than the addition of carbon black alone or the addition of sand alone for increasing the softening temperature. Carbon black was more effective than silica fume for raising the softening temperature of asphalt, but silica fume was more effective for increasing the storage modulus.

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