Improving the Flexural Modulus and Thermal Stability of Pitch by the Addition of Silica Fume

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ABSTRACT: The effects of sand and silica fume on the flexural modulus and thermal stability of pitch were investigated mechanically and thermomechanically. Both modulus and softening temperature were increased by sand addition and further increased by the further addition of silica fume, except that an excessive amount of silica fume caused the modulus to decrease. An effective composition involved 29 vol.% sand and 2 vol.% silica fume.

KEY WORDS: pitch, silica fume, sand, softening, thermal stability, flexural modulus.

INTRODUCTION

PITCH IS THE black or dark-brown residue obtained by distilling coal tar, wood tar, fats, fatty acids, or fatty oils. It is used chiefly as a road tar, in waterproofing roofs and as a matrix precursor for carbon-carbon composites [1–7]. Pitch has a wide range of hardness. It is a brittle substance comprising chiefly aromatic resinous compounds, along with aromatic and other hydrocarbons and their derivatives [8]. In contrast, cement consists of crystalline particles of lime (CaO), silica and alumina held together by a silicate gel. Due to the polymeric nature of pitch and the ceramic nature of cement, pitch is much softer (i.e., lower in stiffness or modulus) and poorer in high temperature resistance (i.e., thermal stability) than cement. The softness is undesirable for structural integrity; the poor thermal stability is undesirable in hot weather conditions. On the other hand, the polymeric nature of pitch renders pitch products better vibration damping ability than cement products. The objective of this paper is to improve the flexural modulus and

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0731-6844/02/01 0091–05 $10.00/0 DOI: 10.1106/073168402024284

thermal stability of pitch by the use of silica fume as an admixture.

Silica fume [9–12] is an admixture in the form of a fine particulate (typically around 0.1 μm particle size) used in concrete for increasing the modulus, strength, abrasion resistance and vibration damping ability and for decreasing the permeability. It has not been previously used for pitch.

EXPERIMENTAL METHODS

The pitch used was 170 Petroleum Pitch from Crowley Tar Products Company, Inc. (New York, NY). Its density was 1.21 g/cm^3. The aggregate used was natural sand of density 2.88 g/cm^3 (as measured by using the Archimedes' Principle). The particle size analysis of the sand (all passing #24 U.S. sieve, 99.9% SiO_2) is shown in Figure 1 of Reference [12]. The sand/pitch ratio was 1.0. The silica fume (Elkem Materials, Inc., Pittsburgh, PA, EMS 965) of density 2.2 g/cm^3 (as measured by using the Archimedes' Principle) was used as an admixture in amounts of 5% and 15% by weight of pitch. All ingredients were mixed by hand at 120°C for 10 minutes.

Other than pitch itself, three pitch-matrix composites were studied. The composites had compositions (by weight ratio) (1) pitch/sand = 1/1 (i.e., 29.6 vol.% sand), (2) pitch/sand/silica fume = 1/1/0.5 (i.e., 29.0 vol.% sand and 1.9 vol.% silica fume), and (3) pitch/sand/silica fume = 1/1/0.15 (i.e., 28.0 vol.% sand and 5.4 vol.% silica fume).

Dynamic mechanical testing at controlled frequencies (0.2, 1.0 and 2.0 Hz) and room temperature (20°C) were conducted under flexure 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 × 15 × 3.5 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 μm (over the minimum value of 5 μm 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.

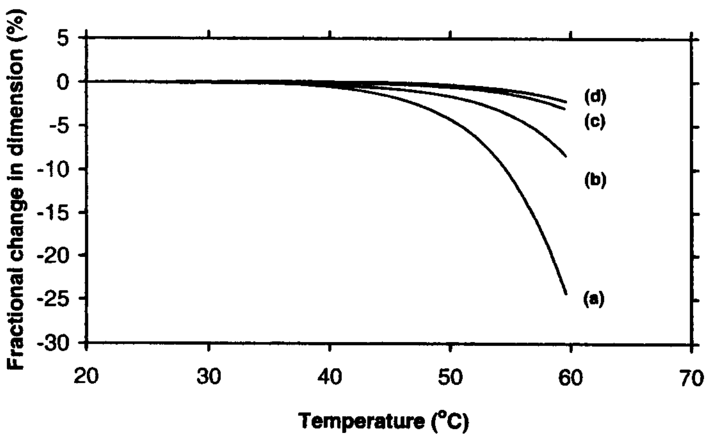

Figure 1. TMA curves of pitch and the mixtures: a, pitch; b, pitch/sand = 1/1; c, pitch/sand/silica fume = 1/1/0.05; d, pitch/sand/silica fume = 1/1/0.15.

Thermal mechanical analysis (TMA) measurement 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) was carried out using a Perkin-Elmer Corp. (Norwalk, CT) Model TMA 7E thermal mechanical analyzer. The heating rate was 2°C/min for the temperature range of 20–60°C. The sample size was 8 × 5 mm in the plane perpendicular to the stress direction and 3 mm in the stress direction. The softening temperature (T_s) 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.

RESULTS AND DISCUSSION

Modulus

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 sand, and the further addition of silica fume (5% by weight of pitch) caused the storage modulus to increase significantly. Both sand and silica fume acted as reinforcements, but the small particle size of silica fume made silica fume effective even in a small amount. As the amount of silica fume increased to 15% by weight of pitch, the storage modulus decreased to a level below that of pitch itself (Table 1). This is attributed to the insufficient amount of pitch binder at high silica fume content. Thus, an excessive amount of silica fume was detrimental.

Table 1. Storage modulus (GPa, ±0.2) of pitch and the mixtures.

Mix	0.2 Hz	1.0 Hz	2.0 Hz
Pitch	0.8	1.2	1.3
Pitch/sand = 1/1	1.3	1.6	1.8
Pitch/sand/silica fume = 1/1/0.05	3.6	4.6	5.1
Pitch/sand/silica fume = 1/1/0.15	0.5	0.8	0.7

Table 2. TMA data of pitch and the mixtures.

Mix	T_s (°C)
Pitch	40.9
Pitch/sand = 1/1	44.2
Pitch/sand/silica fume = 1/1/0.05	49.9
Pitch/sand/silica fume = 1/1/0.15	51.3

Thermal Stability

TMA curves of pitch and pitch-matrix composites are shown in Figure 1. The dimension started to decrease at about 35°C, due to the softening of the pitch matrix. The decrease was largest for pitch itself, was smaller when sand was present and was even smaller when silica fume was also present. The larger the silica fume content, the less was the decrease. These effects are due to the reinforcing ability of sand and silica fume.

The softening temperature (T_s) is shown in Table 2. It was increased by the addition of sand, and was further increased by the further addition of silica fume. As the amount of silica fume content increased, T_s increased.

CONCLUSIONS

The flexural storage modulus and thermal stability of pitch were increased by the addition of sand (100% by weight of pitch). The further addition of silica fume further increased the thermal stability, and if not excessive, further enhanced the modulus also. An excessive amount of silica fume was 15% by weight of pitch. An appropriate amount of silica fume was 5% by weight of pitch. This is because of the insufficient matrix material for binding the ingredients together when the silica fume was excessive.

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BIOGRAPHIES

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