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A TWO-CONTINUOUS-PHASE SULFUR-ASPHALT COMPOSITE—DEVELOPMENT AND CHARACTERIZATION

ANALYZED

by J. J. Beaudoin and P. J. Sereda

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A two-continuous-phase sulfur-asphalt composite—development and characterization

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A two-continuous-phase sulfur-asphalt composite was developed for use as a road repair material. Two methods to obtain a continuous sulfur phase in a continuous asphalt phase are described. Scanning electron microscopy and mercury porosimetry technique provided evidence for a continuous sulfur phase. Mechanical properties—determined from hardness, uniaxial tension, and fracture energy measurements—of the two-continuous-phase sulfur-asphalt composite were studied at 22 and -31°C . Mechanical properties of fiber-reinforced (up to 2% by volume of dacron fibers) sulfur-asphalt composites were also studied.

On a mis au point un composite continu biphasique soufre-asphalte destiné à servir de matériau de réparation routière. L'article décrit deux méthodes qui permettent d'obtenir une phase continue de soufre dans une phase continue d'asphalte. Les techniques de microscopie par balayage électronique et porosimétrie au mercure ont mis en évidence l'existence d'une phase continue de soufre.

A partir d'essais de dureté, de traction simple et d'énergie de fracture, on a étudié les propriétés mécaniques du composite continu biphasique soufre-asphalte à 22 et -31°C . Ont été également étudiées les propriétés mécaniques des composites soufre-asphalte renforcés de fibres (jusqu'à 2% en volume de fibres de dacron).

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[Traduit par la revue]

Introduction

In recent years the availability of large quantities of elemental sulfur in western Canada has generated a resurgence of interest in and research on the utilization of sulfur in construction materials (Sulfur Institute, London 1976; Loov *et al.* 1974; Malhotra 1975).

Numerous investigations have been undertaken and patents filed on sulfur-asphalt systems (Santucci *et al.* 1976; Garrigues *et al.* 1976; Shell Internationale Research Maatschappij N. V. 1966; McConaughay 1973), in which sulfur was distributed as discrete particles acting to improve fluidity for compaction when molten and as a filler when solidified. It was considered possible that a sulfur-asphalt composite could be produced in which the sulfur would form an interconnected network, thus giving the system additional structural rigidity. Such a composite could have interesting possibilities as a repair material for roads damaged by traffic and frost action. It was recognized that for this application, the material should be sufficiently fluid to self-compact and be able to form a good bond with the substrate.

The development undertaken at the Division of Building Research has resulted in the production of a two-continuous-phase sulfur-asphalt composite of unique capability (Beaudoin and Sereda 1978a,b). This paper describes the fabrication, characterization, and properties of this system.

Experimental

Sulfur-Asphalt Composite

A two-continuous-phase sulfur-asphalt system was achieved by using two methods to add the sulfur to liquid asphalt (type III) maintained at 150°C . For both these methods the sulfur-asphalt ratio necessary to produce two-continuous phases was approximately 2.0 by weight.

In the preparation of the composite it is necessary to first obtain a stable emulsion of the liquid sulfur dispersed in liquid asphalt. As the density of sulfur is approximately twice that of asphalt, a very fine droplet size of sulfur must be obtained. The following two methods were found satisfactory to achieve a stable emulsion.

The first method—method A—involved the addition of particulate sulfur ($5\ \mu\text{m}$ diameter) to hot liquid asphalt while stirring continuously to melt the sulfur. The molten mixture could then be cast to the desired shape.

The second method—method B—involved the addition of liquid sulfur maintained at 150°C to the liquid asphalt followed by high-speed mixing (speed is dependent on the geometry of the stirrer blade and mixing vessel) with sufficient shear to form an emulsion of the liquid sulfur in the bituminous material. When the emulsion of sulfur in asphalt, having a sulfur-asphalt ratio of approximately 2, is cooled below the melting point of sulfur, a microporous

continuous crystalline sulfur phase is formed in a continuous viscoelastic bituminous phase. It is this two-continuous-phase system that results in a composite of unique properties; evidence for the existence of a continuous sulfur phase follows.

Evidence for a Continuous Sulfur Phase

(a) Scanning Electron Microscopy

In order to examine the microstructure of the sulfur phase in the mixture and to demonstrate the presence of a continuous sulfur phase, scanning electron microscopy was utilized. The micrographs (Fig. 1) show three different sulfur-asphalt preparations from which the asphalt has been leached using Varsol; samples are approximately 12.5 mm \times 12.5 mm \times 6.2 mm thick. The three sulfur-asphalt preparations are as follows.

(1) Sulfur-asphalt ratio equals 2.0. The sample was prepared by method B. Pore-size distribution data to be presented subsequently showed that method A gives a similar structure.

(2) Sulfur-asphalt ratio equals 2.0. The sample was prepared by manual or slow-speed mixing of liquid sulfur and asphalt at 150°C as in French Patent No. 1,444,629 (Shell Internationale Research Maatschappij N. V. 1966).

(3) Sulfur-asphalt ratio equals 1.0. The sample was prepared by addition of 5 μ m sulfur particles to liquid asphalt at 150°C according to Garrigues' patent, U.S. Patent No. 3,970,468 (Garrigues *et al.* 1976).

Figure 1a shows the continuous porous sulfur network formed in preparation 1 samples. Figure 1b illustrates the *discrete* sulfur particles remaining after asphalt has been leached from preparation 2 samples. The particles are larger than those shown in Fig. 1a and it is apparent that a continuous sulfur network has not formed even though the sulfur-asphalt ratio is 2.0. Figure 1c shows the structure of the sulfur remaining after leaching preparation 3. It has the appearance of a *pile* of sulfur particles, which have formed a close-packed array as a result of structural collapse due to leaching of the asphalt phase.

Sulfur microstructures, as revealed in the micrographs, are consistent with the observations that the mechanical properties for preparation 1 are significantly higher than those for preparations 2 and 3.

(b) Pore-size Distribution of Continuous Sulfur Phase in Samples Prepared by Method A

In order to establish that a continuous sulfur phase had, in fact, been produced the asphalt was extracted from several samples having sulfur-asphalt ratios of 1.5–5.0 using Varsol; extraction time was 2–3 months. The sulfur network at a sulfur-asphalt ratio of 1.5 is very weak as the continuous phase

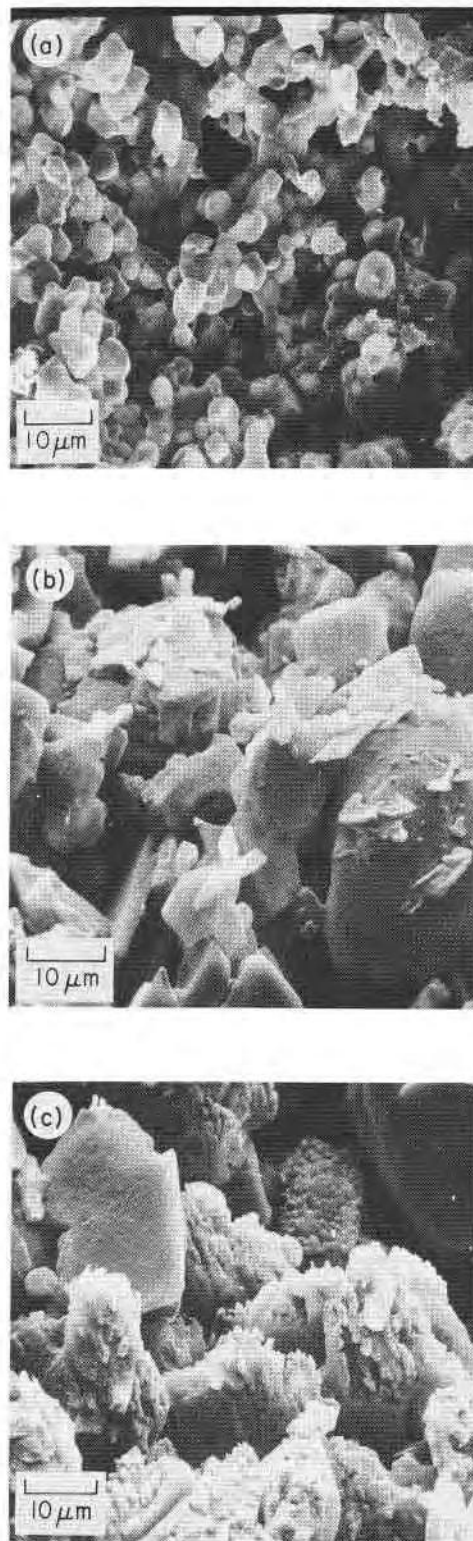


FIG. 1. (a) Preparation 1, sulfur-asphalt = 2.0; (b) preparation 2, sulfur-asphalt = 2.0; and (c) preparation 3, sulfur-asphalt = 1.0.

TABLE 1. Pore-size distribution of continuous sulfur phase

Sulfur-asphalt ratio	Porosity	Pore size (μm)	Remarks	
			(%)	(μm)
1.5	56.0	1-15	81	7-15
2.0	47.5	1-15	90	7-15
2.5	45.0	2.5-15	90	2-10
3.0	44.0	2.5-15	96.5	2-6
5.0	28.5	2.5-15	93	2.5-7

appears to be just beginning to form. Preparations at high sulfur-asphalt ratios required continuous stirring even during casting to avoid segregation of sulfur. Pore-size distributions were determined on the sulfur phase using a mercury porosimeter, at pressures up to 102 MPa. The results are listed in Table 1.

Mechanical Properties of Two-continuous-phase Sulfur-Asphalt Composite

(a) Hardness

Hardness measurements were made on companion samples to those listed in Table 1. The load produced by air pressure in a piston-cylinder arrangement was applied in steps of 13.4 N and the penetration depth was measured at each level after 30 s. A plot of load versus the depth of penetration squared generally

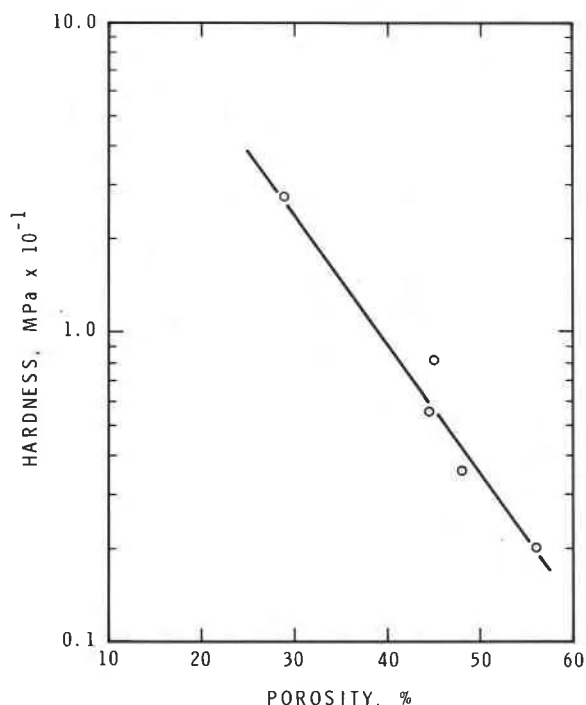


FIG. 2. Sulfur-asphalt composite hardness vs. porosity of sulfur matrix (obtained by extraction of asphalt from the composite).

gave two linear regions with the greater slope for the first part of the penetration. The major number of measurements were made for the deeper penetrations, and the dependence of penetration on load for that condition is believed to represent the hardness of the three-dimensional structures. The hardness is calculated as the applied load per unit area (the circumferential area of the 60° cone in contact with the sample) according to the following formula:

$$H_c = P/2.1h^2$$

where H_c = hardness (MPa); P = load (N); and h = depth of penetration (mm).

In Fig. 2 the logarithm of the hardness of the composite is plotted against porosity of the sulfur matrix after extraction of asphalt. The log hardness decreases as porosity of the continuous sulfur phase increases.

Hardness is plotted against sulfur content of the sulfur-asphalt mixture in Fig. 3. There is a large increase in the slope of the curve in the range in which the continuous sulfur phase begins to form (sulfur-asphalt ratios of 1.5-2.0).

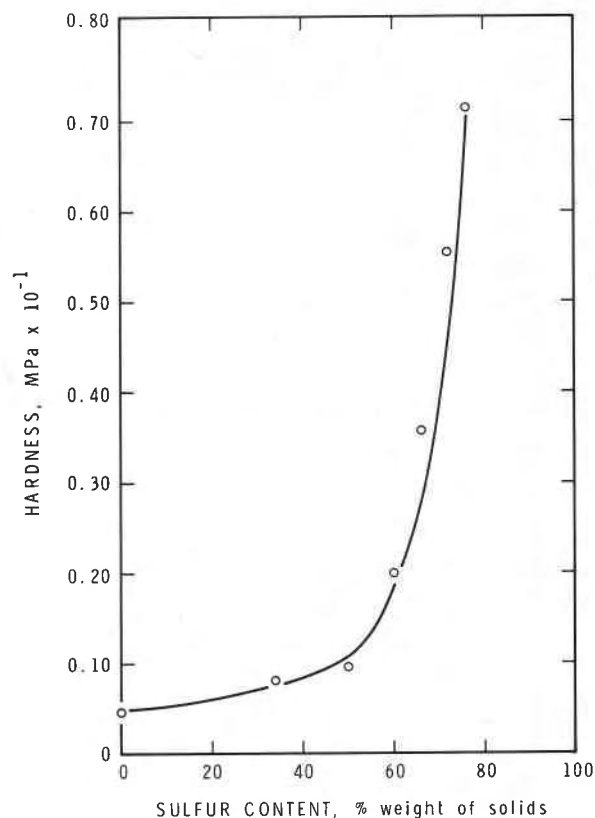


FIG. 3. Hardness vs. sulfur content of sulfur asphalt mixtures.

TABLE 2. Results of tensile tests

Temperature (°C)	Initial tangent modulus of elasticity E_t (MPa)	Sulfur-asphalt ratio	Failure strain $\epsilon_f \times 10^2$	Failure stress σ_f (MPa $\times 10^2$)
22	3.38	0.50	$\gg 4.90$	6
	6.75	1.25	4.90	10
	29.30	1.50	4.45	39
	38.30	2.00	4.17	61
	67.50	2.50	3.11	65
	220.00	3.00	2.76	98
31	29.30	0.50	4.00	100 ± 5
	68.00	1.25	2.66	100 ± 5
	73.50	1.75	2.44	100 ± 5
	87.00	2.00	1.50	100 ± 5
	98.00	2.50	1.10	100 ± 5

(b) Tensile Tests

Uniaxial tension tests were performed on standard tensile specimens (ASTM D638) having cross-sectional areas of 80.6 mm² and gauge lengths of 57.2 mm. Stress-strain curves for various sulfur-asphalt mixtures are plotted in Fig. 4. Crosshead speed was 0.0042 mm/s.

Values of the initial tangent modulus of elasticity, E_t , failure strain, ϵ_f , and failure stress, σ_f , are recorded in Table 2. At 22°C, E_t and σ_f increase with sulfur-asphalt ratio; ϵ_f decreases with sulfur-asphalt ratio. At -31°C, E_t increases with sulfur-asphalt ratio whereas σ_f remains approximately constant; ϵ_f decreases with sulfur-asphalt ratio and has lower values at -31°C than at 22°C for each sulfur-asphalt ratio.

(c) Time-dependent Deformation at Constant Load

Cone area (expressed as circumferential area of

cone penetrometer) at a given time after loading (240 s) decreases as the sulfur-asphalt ratio increases. At sulfur-asphalt ratios between 1.75 and 2.0 an anomalous increase in cone area occurs (Fig. 5). It is postulated that the continuous phase begins to form at these sulfur-asphalt ratios.

With further additions of sulfur, cone area decreases.

(d) Fracture Energy

Work of fracture (and hence an estimate of toughness) was measured using the integral work of fracture method according to the procedure of Tattersall and Tappin (1966). Load-deflection curves using Tattersall-Tappin specimens are plotted in Fig. 6. This procedure cannot be employed if the sulfur-asphalt ratio is less than 1.75 because the material is then viscoelastic. The material becomes brittle when two continuous phases form.

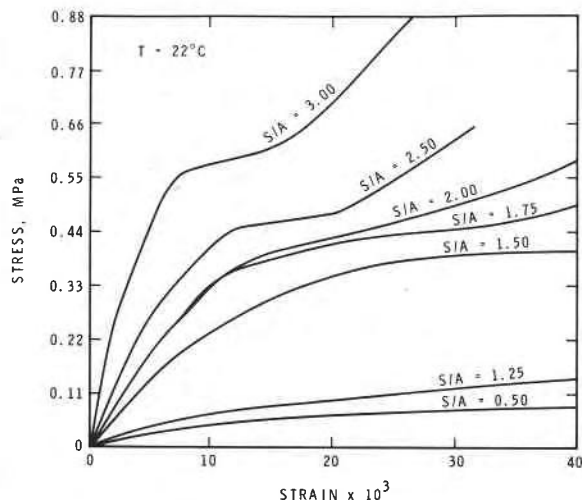
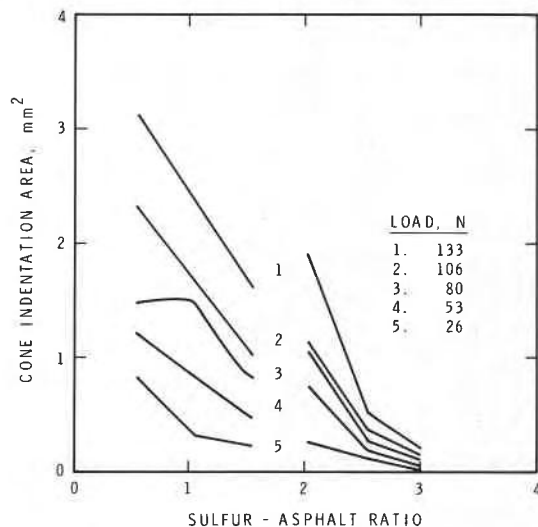


FIG. 4. Sulfur-asphalt composite uniaxial tension tests.

FIG. 5. Cone indentation area of sulfur-asphalt system at $t = 240$ s.

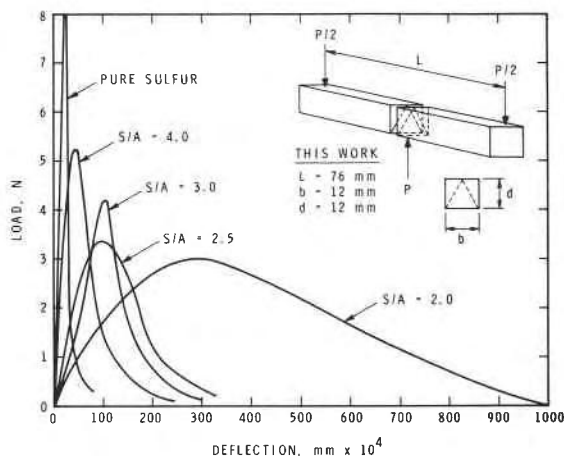


FIG. 6. Load-deflection curves from measurements of integral work of fracture (Tattersall and Tappin 1966).

TABLE 3. Fracture energy of sulphur-asphalt composite

Temperature (°C)	Sulfur-asphalt	Fracture energy (J/m ² × 10 ³)
22	2.0	5.58
	2.5	2.67
	3.0	2.11
	4.0	2.28

Data in Table 3 demonstrate the effect of the sulfur-asphalt ratio on toughness.

Reinforcement of Sulfur-Asphalt Composite Binder

Studies were conducted to ascertain the merits of reinforcing the sulfur-asphalt composite by the inclusion of a relatively small amount (up to about 2% by volume) of a flake and (or) fibrous material. Work with dacron fibers will be reported here. The fibers used were nominally 0.025 mm in diameter and approximately 2.5 mm long.

The following tests were conducted on the fiber-reinforced sulfur-asphalt composite.

(a) Hardness

Figure 7 is a plot of hardness versus fiber content with a matrix material having a sulfur-asphalt ratio of 2. The fiber aspect ratio is varied from 120 to 360 by varying the length of the fibers. Hardness decreases as the aspect ratio increases. Hardness increases as the volume fraction of fiber increases up to a maximum at fiber volume fractions of approximately 1.1–1.35%. This will be discussed later.

(b) Tensile Tests

Stress-strain curves for the sulfur-asphalt composite containing up to 1% by volume dacron fibers are plotted in Fig. 8. The fiber aspect ratio is 120

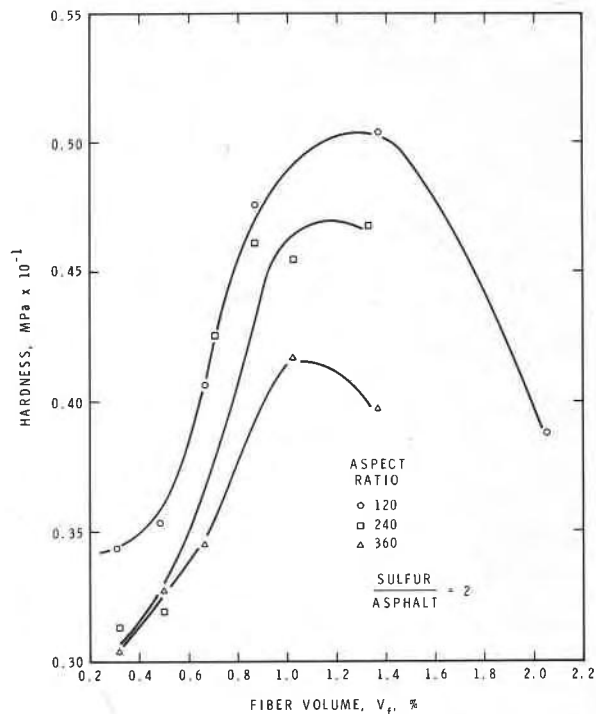


FIG. 7. Hardness vs. fiber volume.

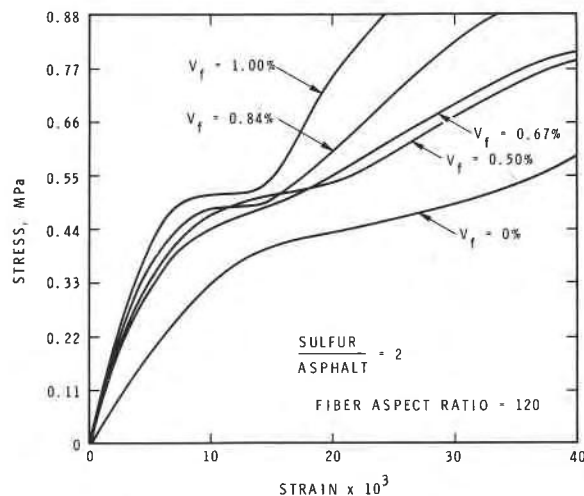


FIG. 8. Reinforced sulfur-asphalt composite uniaxial tension tests.

and the sulfur-asphalt ratio is 2. The initial tangent modulus increases from 38.3 MPa for 0% fibers up to approximately 85.5 MPa for 1% fibers. Tests show that cracking takes place in the sulfur-asphalt matrix followed by stress transfer to the fibers, which themselves ultimately fracture. Presence of fibers up to 1% by volume increases tensile strength up to 30%.

(c) Fracture Energy

Work of fracture measurements clearly show that

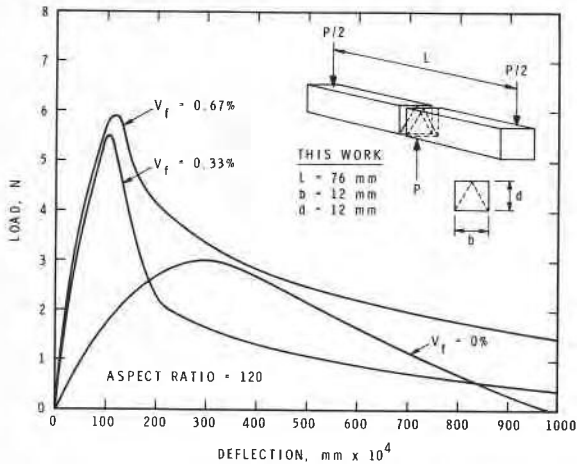


FIG. 9. Load-deflection curves from measurements of integral work of fracture (Tattersall and Tappin 1966).

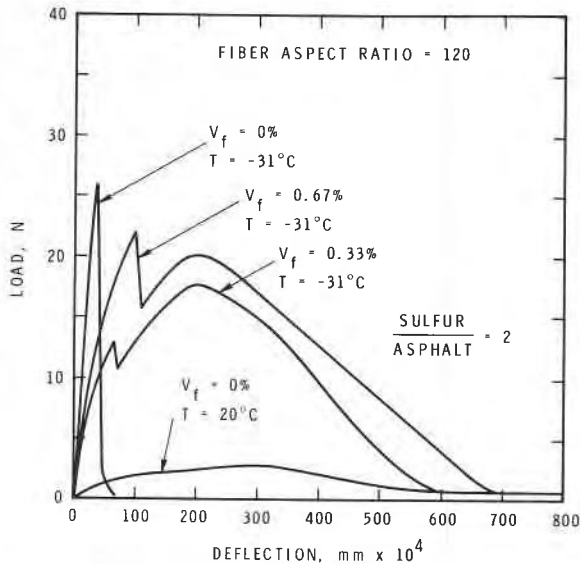
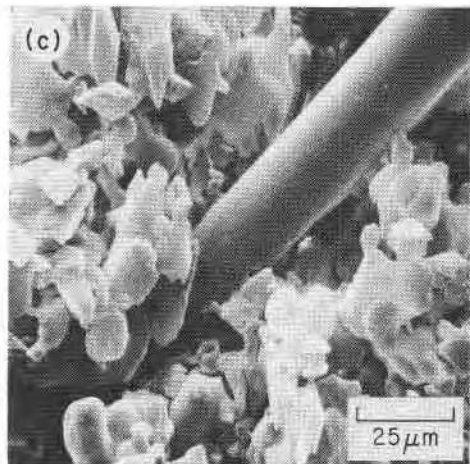
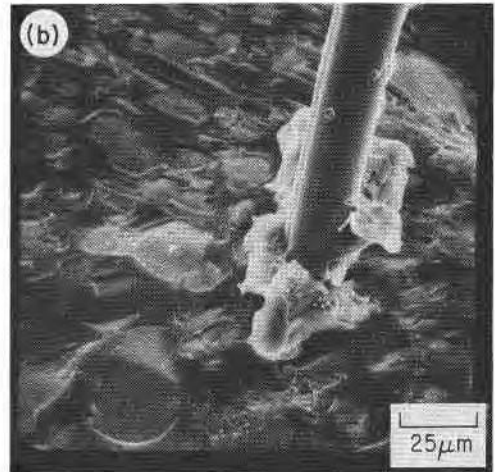
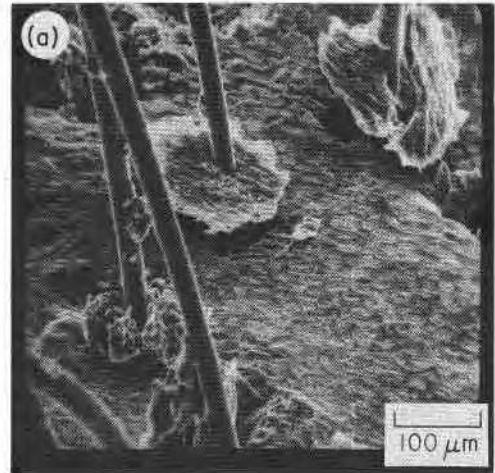


FIG. 10. Load-deflection curves from measurements of integral work of fracture (Tattersall and Tappin 1966).

at 20°C the presence of fibers at volume fractions of 0.67% results in a significant increase in fracture energy of the composite (Fig. 9).

The contribution of the fibers to fracture energy is much greater at -31°C (Fig. 10).

(d) Scanning Electron Microscopy

Fracture surfaces of integral work of fracture specimens were examined by scanning electron microscopy. Ends of fibers remain anchored in the matrix after fracture although partial pull-out has

FIG. 11. (a) Fracture surface fiber-reinforced sulfur-asphalt composite; (b) material adhering to fiber—fiber-reinforced sulfur-asphalt composite; and (c) fiber passing through continuous sulfur network.

occurred (Fig. 11a). Matrix material adhering to the fiber is illustrated in Fig. 11b. In Fig. 11c a fiber passes through the porous sulfur network, revealed using the leaching technique described previously.

Discussion

For the first time in asphalt technology, it has been demonstrated that sulfur can exist as a continuous phase in a sulfur-asphalt mixture. The continuous sulfur phase contributes to the structural rigidity of the composite giving it potential as a repair material. At low temperatures, such as those that are experienced in an average Canadian winter, reinforcing the material with dacron fibers provided a means of increasing the fracture toughness of the composite.

It was observed that hardness was greater for smaller lengths of fiber (lower aspect ratio). This trend has been observed for the compressive strength of steel-fiber-reinforced concrete (Swamy and Mangat 1974). The mechanism of failure of fibers in a compression test is not known. It is known that for hydrated cement systems compressive strength is directly related to hardness (Beaudoin and Feldman 1975) and therefore it might be expected that the mechanism of fiber failure for compressive strength tests is similar to that for hardness measurements.

The failure mechanism of the sulfur-asphalt fiber-reinforced composite is not known. However, as the fibers are embedded in both continuous phases it is apparent that both the sulfur phase and the asphalt phase play a role in the failure process.

The increased stiffness (modulus of elasticity) due to the presence of a small amount of fiber (1% by volume) is not surprising as the modulus of elasticity of dacron fibers (1.02×10^4 MPa) is much greater than the modulus of elasticity of the two-continuous-phase composite (0.38×10^2 MPa). The use of mixture rules to predict the modulus of elasticity of the fiber-reinforced composite with and without the addition of fillers and aggregates will be discussed in another paper.

Studies on the application of the reinforced sulfur asphalt composite to road repair and performance requirements for such application will be reported later.

Conclusions

1. A two-continuous-phase sulfur-asphalt composite has been developed.

2. The continuous sulfur network formed when the sulfur-asphalt ratio was approximately 2.0 increases the hardness and tensile strength of the composite.

3. Toughness, modulus of elasticity, tensile strength, and hardness of the sulfur-asphalt composite are increased by the addition of up to 1% by volume of dacron fibers. The increase in these properties is significant at temperatures as low as -31°C .

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- BEAUDOIN, J. J., and FELDMAN, R. F. 1975. A study of mechanical properties of autoclaved calcium silicate system. *Cement and Concrete Research*, **5**, pp. 103-118.
- BEAUDOIN, J. J., and SEREDA, P. J. 1978a. Reinforced sulfur-asphalt composites. U.S. Patent Application No. 927,362.
- 1978b. Reinforced sulfur-asphalt composites. Can. Patent No. 1,042,610.
- GARRIGUES, C., SIGNOURET, J. B., and CHAMBU, C. 1976. Sulfur emulsion in bituminous material. U.S. Patent No. 3,970,468.
- LOOV, R. E., VROOM, A. H., and WARD, M. A. 1974. Sulfur concrete—a new construction material. *Journal of the Prestressed Concrete Institute*, **19**(1), pp. 86-95.
- MC CONNAUGHAY, K. E. 1973. Pavement and method of making it. Can. Patent No. 993,706.
- MALHOTRA, V. M. 1975. Development of sulfur-infiltrated high-strength concrete. *Journal of the American Concrete Institute*, **72**(9), pp. 466-473.
- SANTUCCI, L. E., CAMPBELL, R. W., and WOO, L. 1976. Sulfur composition. U.S. Patent No. 3,997,355.
- SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N. V. 1966. Composition Bitumineuse de Revêtement Routier. Fr. Patent No. 1,444,629.
- SULFUR INSTITUTE, LONDON, (editor). 1976. International Symposium on New Uses for Sulfur and Pyrites, Madrid, Spain.
- SWAMY, R. N., and MANGAT, P. S. 1974. Influence of fiber geometry on the properties of steel fiber reinforced concrete. *Cement and Concrete Research*, **4**, pp. 451-465.
- TATTERSALL, H. G., and TAPPIN, G. 1966. Work of fracture and its measurement in metals, ceramics and other materials. *Journal of Materials Science*, **1**(3), pp. 296-301.