Engineering Properties of First Generation Plasticized Sulfur Binders and Low Temperature Fracture Evaluation of Plasticized Sulfur Paving Mixtures

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ABSTRACT

The low temperature fracture potential, fatigue potential, and deformation characteristics of first generation plasticized sulfur binders in paving mixtures are discussed. Fracture mechanics techniques were used in the characterization of these materials. Recommendations, based on properties of first generation materials, for improvement of the engineering behavior of second generation plasticized sulfur binders in paving mixtures are presented. Plasticized sulfur binders are promising new materials; however, low temperature fracture sensitivity is a problem that must be overcome before these binders can be used in cold climates or regions susceptible to rapid temperature drops. Rheological testing has illustrated the temperature sensitivity of plasticized sulfur binders and the need to consider this sensitivity in design applications. The fracture mechanics techniques and parameters defined and discussed in this paper are recommended as criteria to be used in the development of plasticized sulfur mixtures with improved low temperature fatigue fracture properties.

Plasticized sulfur has been extensively investigated by the Federal Highway Administration (FHWA) during the past 8 years. During this period, a first generation of plasticized sulfur binders has been developed and their role as a total replacement for asphalt cement in paving mixtures carefully researched. Texas A&M University and Matecon, Inc., of Oakland, California, under contract to FHWA have characterized first generation binders from both a chemical and an engineering standpoint. This characterization has revealed certain deficiencies in these first generation binders. Overcoming these deficiencies was the goal in the development of a second generation of plasticized sulfur binders. Texas A&M and Matecon under contract with FHWA are developing a second generation of plasticized sulfur binders.

To date some 100 formulations of hydrocarbon plasticizers and elemental sulfur have been produced in laboratory batches and screened for potentially acceptable performance. Of these 100 formulations, 10 have been accepted for full-scale investigation. This investigation includes (a) the production of these binders in 25-gal batches in pilot plant reaction vessels at Texas A&M, (b) characterization of low temperature fracture susceptibility, (c) characterization of flexural fatigue, (d) characterization of permanent deformation potential, and (e) evaluation of production and storage stability.

The engineering testing program to characterize the second generation binders was developed on the basis of the experience of the first generation study. This is especially true of the low temperature fracture study in which the basic principles of fracture mechanics were employed together with nontraditional testing procedures.

A summary of the major findings of the characterization study of first generation plasticized sulfur binders is presented. The presentation of these findings will be followed by a discussion of the present development of improved second generation binders based on (a) deficiencies identified in first generation binders and (b) nontraditional testing techniques developed in the first generation study.

NATURE OF SULPHLEX

Background

In June 1980 Southwest Research Institute reported the development of four formulations of plasticized sulfur binders called Sulphlex (1). These four binders were selected from the testing of approximately 450 different formulations of elemental sulfur and plasticizers. Sulphlex is a trade name for a family of pavement binders composed of chemically modified sulfur.

It was initially recognized that if sulfur were to be used as a pavement binder, it would have to exhibit more plastic characteristics. The term plasticized sulfur is often used to describe the modification of sulfur to achieve the characteristics of flexibility, workability, and extensibility.

It has long been known that when elemental sulfur is heated to above its transition temperature and rapidly quenched at approximately 70°F, it exhibits a plastic character. However, as the material cools to "room" temperature, it quickly hardens with the formulation of orthorhombic $S_8$ sulfur crystals. Evidence exists that above $320°F$ molten sulfur consists of a mixture of $S_8$ rings and $S_x$ chains where the value of $x$ can be extremely large. Exactly how the plasticization occurs at this point is uncertain and speculative. In any case the mechanism
of plastic sulfur is brought about by a physical change that does not lend itself to practical application in the preparation of binders for paving.

What must be done to retain the desirable behavior of the plasticized sulfur is to convert the sulfur to a plastic by a chemical reaction, a mechanical change, or a combination of these. Before the research performed for the Federal Highway Administration by Southwest Research, efforts at plasticization had dealt with a single additive. The Sulphlex mixtures are based on the reaction of multiple additives with elemental sulfur. Once reacted, all of the Sulphlex formulations resemble asphalt in terms of their handling characteristics.

The Sulphlex binder formula 233, which was reported to possess properties similar to asphalt concrete both during the construction process and in the pavement layer, is discussed.

Composition and Chemistry

Sulphlex 233 is a manufactured product. Specifically, molten, elemental sulfur is reacted in a vessel at 300°F with a blend of plasticizers or chemical modifiers: dicyclopentadiene (DCPD), vinyl toluene, and dipentene. The formulation of the 233 binder is 70 percent by weight of elemental sulfur, 12 percent DCPD, 10 percent dipentene, and 8 percent vinyl toluene.

Raw Materials and Formulation

At the beginning of this project it was agreed that work should be started with the Sulphlex 233 formulation and preparation procedure and that the raw materials used in the preparation of laboratory and pilot plant batches should be as pure as it is possible to obtain from commercial sources.

The chemical structures of the reactants of Sulphlex 233 are shown in Figure 1. Two of the reactants, DCPD and dipentene, are diolefins that have two double bonds for potential reaction with sulfur. Vinyl toluene has one double bond. All of these ingredients, except the dipentene, are of relatively high purity. The specific dipentene used in this work has the highest purity of the dipentenes that are commercially available.

FIGURE 1 Structures of Sulphlex raw materials.

Process Variables

The Sulphlex production process requires considerable study of the variables that are involved in order that specifications can be set and reproducible products can be made. In the case of Sulphlex 233, four raw materials, which can interact with one another in a variety of ways depending on the reaction conditions, are involved. The variations in properties among different lots of Sulphlex 233 are quite apparent. Without changing the basic formulations there are a number of variables involved, such as

1. Temperature,
2. Time,
3. Pressure,
4. Stirring,
5. Reactor size,
6. Order of addition of raw materials, and
7. Slight deviations in the ratios of the reactants in the charge.

Variations in Temperature and Time of Reaction

Table 1 gives the formulation and reaction times and temperatures used to produce the first generation Sulphlex binders studied. The CR series binders were produced at Cal-Resin of Vallejo, California, and binder 233A was produced at Texas A&M. All binders were produced in similar reaction vessels as explained elsewhere.

Sulphlex 233 prepared at 338°F is a very different product from Sulphlex 233 prepared at 284°F or 302°F (all products with a 6.5 hr reaction time). The product prepared at 338°F is more thermally stable and changes less on further heating. However, the product is initially low in viscosity (compared to products produced at lower temperatures), but much of the free sulfur soon crystallizes resulting in a hard product that remains unchanged on further standing. From the hardness of the crystallized material, the 338°F product would appear to produce a paving material more like portland cement than asphalt concrete.

The Sulphlex 233 made at lower temperatures, 284°F or 302°F, is more like asphalt. Initially it is more viscous than the 338°F product, but on storage at room temperature it remains a viscous, one-phase product much longer. This indicates that the free sulfur crystallizes out more slowly. The product made at the lower temperatures is not as thermally stable in the sense that on further heating the properties change and approach those of the 338°F product.

ENGINEERING PROPERTIES—MIXTURE DESIGN

The first step in the Sulphlex mixture characterization was to establish an acceptable mixture design procedure. It was established through a factorial study of mixture fabrication variables that Sulphlex can be fabricated identically to asphalt concrete in the laboratory. However, the behavior of Sulphlex was quite different. Sulphlex exhibited Marshall stabilities 50 to 100 percent higher than those of comparable control asphalt concrete mixtures with equal binder contents by volume. However, an unmistakable trend of high Marshall flows (about twice as high as for identical control asphalt concrete mixtures) was exhibited for Sulphlex even though concomitant stabilities were much greater.

The significantly different mixture behavior of Sulphlex mixtures resulted in the search for a new
A fracture approach (different from Marshall or Hveem that are based on historic asphalt concrete performance) to Sulphlex mixture design. The approach selected employs strain energy density and a stress-strain failure envelope developed over a range of test temperatures and durations of loading. The mode of testing is the indirect tensile test, which in recent years has been extensively researched and is easily accessible to state and federal agencies.

The Sulphlex mixture design procedure used in this study was based on the failure envelope-strain energy density concept discussed elsewhere. All mixtures discussed in this paper were designed according to this failure envelope-strain energy concept.

FRACTURE STRENGTH

Background

The available data suggest that fracture strength of asphalt concrete under low temperatures or rapid loading rates, or both, is at its highest level, but fracture occurs at small strains. Plan (5) defined the limiting strain for asphalt concrete at relatively low temperatures to be approximately $1.0 \times 10^{-5}$ in. per inch. This is about one order of magnitude greater than allowable strain levels in fatigue loading.

The critical condition for fracture in asphalt concrete occurs at low temperatures or rapid loading rates, or both. It is here that the asphalt behaves in a most brittle manner. Stiff mixtures are susceptible to low temperature fracture induced during cooling, even if they possess high fracture strength, because of the high stresses. Sulphlex is an extremely stiff material. Therefore it was quite logical to be concerned about its potential for low temperature cracking.

Research Approach

Two approaches were used to evaluate the low temperature fracture potential of Sulphlex binders: (a) the traditional fracture strength versus induced stress approach and (b) a fracture mechanics-based approach employing the J-integral.

The traditional approach is sound provided that the laboratory-measured fracture strengths accurately describe what occurs in the field. Unfortunately, the indirect tensile test has limitations. Rigid assumptions are made that describe the method of load application and the behavior of the material during load application (linearly elastic) (6). These assumptions are, to at least some degree, violated during every test. Therefore, the test provides at best an estimate of fracture strength.

The J-integral, a measurement of fracture toughness in an elastic-plastic material, was used as an alternate approach to the low temperature fracture problem.

The critical value of J-integral, termed $J_{RC}$, may be found by the method established in ASTM E 813. The critical $J_{RC}$ is the energy required to drive a sharp-tipped crack or the energy released as the sharp crack tip propagates.

Bend specimens of the type shown in Figure 2 and described in ASTM E 813 were used. As the specimens were loaded monotonically at the midpoint, a linear variable transformer (LVDT) recorded the crack opening displacement. A load displacement plot was recorded. The area within the plot of load versus displacement was computed and used in the calculation of the J-integral with crack growth. Crack length progression may be followed by several techniques. The most common way is to relate the crack length to the change in compliance of the beam with crack growth. A less common but more accurate way to measure crack growth is by a "KRAK gage" (7) that is bonded to the specimen. The crack progresses and tears the metal foil gauge changing the electrical resistance monitored across the gauge resulting in an extremely accurate measure of crack growth. The "KRAK gage" was used in this research.

It is not practical to use bend specimens to compute $J_{RC}$ values at temperatures much above $T_g$. This is because the material begins to behave plastically and visously to the point where the prop-

### TABLE I Formulation and Processing Conditions for Sulphlex Binders Analyzed in this Study

<table>
<thead>
<tr>
<th>Binder Identification</th>
<th>Formulation*</th>
<th>Reaction Temperature (°F)</th>
<th>Reaction Time (hr)</th>
<th>Penetration at 77°F (1 day old), dmm</th>
<th>Viscosity at 275°F (1 day old), poises</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR1</td>
<td>68% sulfur, 12% DCPD, 12% DP, 8% vinyl toluene, Sulphlex catalyst (1% of mix)</td>
<td>302</td>
<td>6.5</td>
<td>35</td>
<td>10.2</td>
</tr>
<tr>
<td>CR2</td>
<td>70% sulfur, 12% DCPD, 10% DP, 8% vinyl toluene, Sulphlex catalyst (1% of mix)</td>
<td>338</td>
<td>6.5</td>
<td>165</td>
<td>4.0</td>
</tr>
<tr>
<td>CR3</td>
<td>70% sulfur, 12% DCPD, 10% DP, 8% vinyl toluene, Sulphlex catalyst (1% of mix)</td>
<td>302</td>
<td>6.5</td>
<td>22</td>
<td>5.8</td>
</tr>
<tr>
<td>CR5</td>
<td>70% sulfur, 12% DCPD, 10% DP, 8% vinyl toluene, Sulphlex catalyst (1% of mix)</td>
<td>320</td>
<td>6.5</td>
<td>78</td>
<td>2.5</td>
</tr>
<tr>
<td>233A</td>
<td>68% sulfur, 12% DCPD, 10% solvenol, 10% vinyl toluene, Sulphlex catalyst (1% of mix)</td>
<td>300-350</td>
<td>4.5</td>
<td>40</td>
<td>11.0</td>
</tr>
</tbody>
</table>

*Expressed as percentage by weight.
gation of a sharp tipped crack in this bend specimen geometry is not possible because the area of the plastic zone ahead of the crack tip is too large relative to specimen geometry. However, at temperatures near or below $T_g$, the test works well.

The parameters $J_{IC}$ were computed for AC-10, CR1, CR2, CR3, CR5, and 233 over a range of temperatures. These values are given in Table 2.

**TABLE 2** Summary of $J_{IC}$ Values Versus Temperature

<table>
<thead>
<tr>
<th>Binder</th>
<th>$T_g$ ($^\circ$F)</th>
<th>Test Temperature ($^\circ$F)</th>
<th>$J_{IC}$ (ft/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-10</td>
<td>-20</td>
<td>-30</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>-15</td>
<td>-15</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>+20</td>
<td>+20</td>
<td>0.38</td>
</tr>
<tr>
<td>CR5</td>
<td>+20</td>
<td>+5</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>-15</td>
<td>-15</td>
<td>0.35</td>
</tr>
<tr>
<td>CR2</td>
<td>+20</td>
<td>0</td>
<td>0.27</td>
</tr>
<tr>
<td>CR3</td>
<td>+20</td>
<td>0</td>
<td>0.29</td>
</tr>
<tr>
<td>233</td>
<td>+20</td>
<td>0</td>
<td>0.29</td>
</tr>
</tbody>
</table>

$T_g$ values are based on differential scanning calorimetry.

Results of Fracture Mechanics Analysis

Differential scanning calorimetry (DSC) analyses identified the glass transition temperature of all Sulphlex binders tested in this study (CR1, CR2, CR3, CR5, and 233) as being substantially above that of asphalt concrete (approximately 30°F above) (Table 2). This can also be predicted simply by observing the creep compliance, stiffness, or resilient modulus data from Sulphlex and asphalt concrete mixtures. These relationships clearly illustrate the occurrence of a glassy plateau at much higher temperature for Sulphlex than for asphalt.

The $J_{IC}$ values for AC-10 and Sulphlex CR5 and CR1 mixtures were determined at or near the $T_g$. No tests were made above $T_g$, but it is hypothesized that fracture toughness will increase dramatically above $T_g$. It may be predicted that $J_{IC}$ should be relatively constant below $T_g$.

Of greatest practical importance is that at any specific low temperature (say below freezing, 32° F), the $J_{IC}$ or toughness is substantially greater for the AC-10 mixtures tested than for the Sulphlex mixtures tested.

That Sulphlex has a glass transition at a much higher temperature than does asphalt suggests that low temperature cracking is inevitable in cold climates subject to rapid temperature drops. Strain energy densities (computed from indirect tensile test data) of asphalt concrete and Sulphlex will become at least comparable within the midrange of temperatures that most often affect pavements. Thus Sulphlex would be expected to behave much more favorably compared with asphalt concrete in flexural load-controlled fatigue at the traditional midrange temperature, 70° F or 68° F, than in resistance to displacement-controlled fracture at low temperatures. This conclusion is substantiated by the results presented in this paper.

**FATIGUE FRACTURE**

The fatigue-fracture behavior of pavement materials has been under intensive study for the past two decades. The studies can be placed into two distinct categories: phenomenological and mechanistic.

**Phenomenological Approach**

This approach was developed by Monismith et al. (8), Pell and McCarthy (9), and Kaasbom (10). Fatigue life ($N_f$) is defined to be inversely proportional to the maximum tensile strain ($\epsilon_t$) in the form of a power law:

$$N_f = K_1 (1/\epsilon_t)^{K_2}$$  \hspace{1cm} (1)

where $K_1$ and $K_2$ are regression constants.

In general, the phenomenological approach has provided a reasonably simple procedure that has been widely adopted. However, it bears the limitation that it cannot take into account both crack initiation and propagation. Such a differentiation may be quite important in estimating fatigue life. If a pavement material is brittle, the time required to initiate the crack will constitute the major portion of its fatigue life and crack propagation will be rather rapid. On the other hand, as the pavement material becomes more ductile, the time needed to propagate the crack to failure will constitute an increasing portion of the fatigue life of the pavement.

Results of Phenomenological Fatigue Study

Phenomenological fatigue parameters $K_1$ and $K_2$ for the Sulphlex and the asphalt concrete control mixture are given in Table 3. These regression parameters are the result of controlled stress fatigue testing and represent the regression relationship between initial tensile strain at the 200th load application and the number of load applications to failure. Figure 3 shows initial strain versus load applications to failure based on controlled stress testing for AC-10 and CR5 mixtures for testing temperatures of 40°F, 70°F, and 100°F.

On the basis of the data presented in Table 3 and Figure 3 the following observations are made:

1. In controlled-stress flexural beam fatigue, Sulphlex CR5 performs comparably to AC-10 at 70°F in mixtures with crushed limestone.
TABLE 3 Summary of Ki and K2 Values from Phenomenological Beam Fatigue Testing

<table>
<thead>
<tr>
<th>Material</th>
<th>Ki Line (°F)</th>
<th>K2 Line (°F)</th>
<th>Test Temperature (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-10 mixture</td>
<td>7.26 x 10^{-11}</td>
<td>3.90</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>8.00 x 10^{-9}</td>
<td>3.74</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>5.60 x 10^{-7}</td>
<td>3.60</td>
<td>0.82</td>
</tr>
<tr>
<td>CR1 mixture</td>
<td>2.30 x 10^{-6}</td>
<td>2.88</td>
<td>0.80</td>
</tr>
<tr>
<td>CR2 mixture</td>
<td>3.49 x 10^{-5}</td>
<td>2.53</td>
<td>0.50</td>
</tr>
<tr>
<td>CR3 mixture</td>
<td>1.73 x 10^{-6}</td>
<td>4.43</td>
<td>0.69</td>
</tr>
<tr>
<td>CR5 mixture</td>
<td>1.74 x 10^{-7}</td>
<td>3.39</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>2.12 x 10^{-9}</td>
<td>3.50</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>1.25 x 10^{-5}</td>
<td>3.29</td>
<td>0.75</td>
</tr>
</tbody>
</table>

2. Temperature has a similar effect on Sulphlex CR5 and on AC-10. The fatigue performance of Sulphlex CR5 deteriorates more rapidly as temperature drops (70°F to 40°F) than does the fatigue performance of AC-10 under the same temperature drop.

3. Sulphlex binders CR5 and CR3 are superior to binders CR1 and CR2.

On the basis of the controlled-stress phenomenological study, Sulphlex mixtures composed of binders CR5 and possibly CR3 should perform comparably to asphalt concrete in thick pavements where flexural response to which is controlled stress. To more fundamentally evaluate the effects of temperature and cyclic fracture potential, the concepts of fracture mechanics were utilized.

Mechanistic Approach

The mechanistic approach presented by several researchers (11-13) considers fatigue as a process of cumulative damage and uses fracture mechanics principles. The most common mechanistic model is the Paris equation

$$\frac{dc}{dN} = A(\Delta K)^n$$

(2)

This equation relates the rate of crack growth (dc/dN) to the induced stress intensity factor (K) in a form of power law. With the knowledge of material properties A and n, Equation 2 can be integrated over a given range of crack length to calculate fatigue life (Nf):

$$N_f = \frac{c_f - c_0}{A^2(1/n)^2} \int \frac{dc}{A(K^n)}$$

(3)

where \(c_0\) is initial crack length, \(c_f\) is final crack length, and K is cyclic zero-to-tension loading.

At a constant loading amplitude (σ), K is defined as

$$K = \sigma (a_0^{1/2})$$

(4)

Combining Equations 3 and 4 and performing the integration yields

$$N_f = \frac{2}{(2-n)A^2n/2} \left[ \frac{c_f^{(1-n/2)} - c_0^{(1-n/2)}}{(1-n/2)} \right]$$

(5)

In 1973 Schapery presented his "Theory of Crack Growth in Visco-elastic Media" (14) in which he showed the theoretical basis for application of Paris' law. He derived an equation relating the velocity of crack growth in visco-elastic material, due to mode I displacement, to the fatigue-fracture properties of that material, A and n.

Germann and Lytton (15) investigated the effects of mixture variables on material properties A and n. The device used in testing was called the Overlay Tester because it applied a constant displacement to samples, which simulated the cyclic thermally induced movements of cracks below pavement overlays. The Overlay Tester was used in this research to evaluate fracture mechanics parameters. In the Overlay Tester, 3 in. x 3 in. x 15 in. beams of Sulphlex and asphalt concrete were subjected to cyclic constant displacements of 0.02 in. The energy required to produce the constant displacement per cycle was recorded based on a method developed by Balbissi (16).

Balbissi (16) found that the J-integral, a measure of elastic-plastic energy release per area of crack extension, could be used in the Paris equation in lieu of the change in stress intensity factor.
The term $J^*$ is used in lieu of $J$ because the $J$-integral term does not account for unloading but is specifically applicable only to a condition of monotonic loading (no unloading).

Of course, it is no surprise that $J^*$ provides a much superior model of crack growth in the Paris equation than does the use of $K_T$. This is because $J^*$, as previously explained, accounts for the elastic-plastic nature of the material ahead of the crack tip whereas $K_T$ accounts only for linear elastic conditions.

### Results of Fracture Mechanics Approach

Figure 4 shows a summary of the $dc/dN$ versus $J^*$ relationships for mixtures of crushed limestone with binders CR3, CR5, or AC-10. In displacement control, a large crack growth rate occurs initially and the rate slows as the crack propagates.

In general, a more brittle material in Figure 4 would plot above and would be steeper than a relatively ductile material. Thus the relative fatigue fracture propagation potential can be evaluated on the basis of the relative position of the plots in Figure 4 and of the $A^*$ and $n^*$ regression constants given in Table 4.

From Figure 4 several conclusions were drawn:

1. At 68°F the asphalt concrete mixtures are significantly less brittle than are the comparable Sulphlex mixtures (CR3 or CR5).

2. Although the CR3 mixture appears to be more brittle than the CR5 mixture, the differences are not significant.

3. The temperature effects on the fatigue relationships are substantially greater for the Sulphlex binders than for the asphalt concrete binders. A temperature variance of 19°F (77°F to 58°F) for asphalt concrete produces a relatively small, though certainly detectable, variance in fatigue properties. However, a variance of only 12°F (77°F to 65°F) produces a substantial variance in Sulphlex (CR5) fatigue properties. This sensitivity to controlled-strain or controlled-displacement fatigue is apparent for Sulphlex mixtures.

4. Although CR5 mixtures may be comparable to asphalt concrete in terms of fracture propagation properties at 77°F, asphalt concrete is clearly superior at lower temperatures--as little as 12°F lower.

A hybrid term combining parameters $A$ and $n$, in Paris' law, was suggested by Pickett and Lytton (17), which accounts for the effects of both parameters in fatigue-fracture behavior. In this approach the term $(n + \log A)$ is defined as a measure of resistance to crack growth. This parameter will always be negative; the smaller (more negative) this parameter, the greater is the crack resistance of the material. On the basis of the $(n^* + \log A^*)$ parameter, which is the analogous form when $J^*$ is used (Equation 6) in lieu of $K$, the superior fatigue performance potential of the control asphalt (AC-10) is apparent (Table 4).

### Deformation Analysis

Creep testing in accordance with FHWA's VESYS User's Manual (18) was performed on Sulphlex and the as-
phalt concrete control mixtures. The compliance curves were transformed into stiffness versus duration of load plots because this relationship is normally more meaningful to highway engineers. These plots are shown in Figure 5. From these plots the following observations are made:

1. The glassy plateau for Sulphlex mixtures begins at a much higher temperature than for the asphalt concrete.
2. Stiffnesses are much higher for Sulphlex than for asphalt concrete for durations of load typical of moving wheel loads.
3. At long durations of load, >10^6 sec, Sulphlex binders exhibit a linear amorphous polymeric degradation in stiffness.
4. The slope of the transition portion of the stiffness versus load duration master curves is statistically significantly less for the control asphalt concrete mixture than for the Sulphlex mixtures.
5. The glassy modulus of the Sulphlex CRS mixture is statistically significantly less than that of other Sulphlex mixtures but significantly greater than the glassy modulus for the control mixtures of asphalt concrete.

**MODULUS PROPERTIES**

In this study the modulus properties of Sulphlex were measured by five methods:

1. Resilient modulus ($E_r$),
2. Creep stiffness,
3. Dynamic modulus ($E'$),
4. Flexural modulus, and
5. Relaxation modulus.

In this paper, only the resilient modulus results are presented (Figure 6). However, the general trends shown were substantiated by the other forms of modulus testing.

The resilient moduli, defined as the ratio of induced stress to recoverable strain, were measured by the Mark IV device developed by Schmidt (19). The device applies a 0.1-sec load pulse once every 3 sec across the vertical diameter of a cylindrical specimen (Marshall type specimen) and senses by linear variable transformers the resultant deformation across the horizontal diameter. Laboratory mixtures prepared with binders CR1, CR2, CR3, CR5, 233A, and AC-10 were aged for 6 days at 50°F and tested at four temperatures: -10°F, 32°F, 73°F, and 104°F. The
6-day cure period was selected on the basis of an aging study that revealed that the resilient modulus does not appreciably change in the laboratory following 6 days of curing at 50°F. In addition to the laboratory-molded specimens, field cores from a Sulphlex demonstration project in San Antonio, Texas, (Loop 1604) were tested over the same temperature range. These data are plotted in Figure 6.

The resilient modulus versus temperature relationship is similar for Sulphlex binders CR1, CR2, and CR3 and the field cores from Loop 1604, San Antonio, Texas. These cores were 2 months old at the date of testing. The mixtures with CRS and the original 233A (laboratory molded) proved to have significantly lower resilient moduli than the other Sulphlex binders across the test temperature range.

Both the laboratory mixture of AC-10 plus crushed limestone and the field cores from Loop 1604 of AC-20 and crushed limestone produced similar M R versus temperature relationships. It is clear that the Sulphlex mixtures are substantially stiffer across the temperature range. Obviously, resilient moduli will vary according to the effects of aggregate type, gradation, void content, and so forth, but the unmistakable trend is that Sulphlex mixtures under rapid load rates are much stiffer than asphalt concrete. However, Sulphlex binders display a definite temperature susceptibility and viscoelastic response.

Figure 6 indicates that the viscoelastic behavior of Sulphlex actively begins at about 32°F. Below about 32°F the modulus is probably very nearly linearly elastic. The resilient modulus data in Figure 6 coupled with stiffness data in Figure 5 indicate a dominating viscous response at high temperatures, perhaps above 100°F.

The argument has often been put forth that Sulphlex layers should be designed as rigid pavement layers because they probably crystallize rapidly in the thin film arrangement found in mixtures, and they are probably very nearly linearly elastic in normal pavement conditions. However, the pronounced viscous effects at higher temperatures and longer loading rates and especially a combination of the two effects demand thoughtful consideration of the consequences of these effects in pavement design applications.

CONCLUSIONS AND RECOMMENDATIONS

On the basis of the research accomplished in the study, the following conclusions are enumerated:

1. Sulphlex binders are capable of producing mixtures with characteristics which are similar to those of asphalt concrete.

2. The thermal stability and engineering behavior of Sulphlex is highly dependent on the plasticizers used as well as production process variables such as reaction time and temperature.

3. First generation Sulphlex mixtures are generally more brittle and thus more susceptible to fatigue cracking than similar mixtures of asphalt concrete. However, second generation binders that demonstrate much-improved fatigue fracture performance are under development.

4. The combination of high glass transition temperatures and low JIC values at or near the Tg makes Sulphlex binders susceptible to cracking at low temperatures or to thermally induced fatigue. However, once again, certain second generation Sulphlex binders demonstrate much-improved low temperature behavior.

5. Sulphlex mixtures are much less compliant than comparable asphalt concrete mixtures except at very long (10⁶ sec or greater) load duration. At very long load durations or very high temperatures, or both, Sulphlex binders and mixtures exhibit a degradation resulting in a quite noticeable increase in compliance (or reduction in stiffness) compared with the control asphalt concrete.

6. First generation Sulphlex mixtures are substantially stiffer than asphalt concrete over the temperature range normally encountered but possess a substantial temperature sensitivity.

Although a lengthy list of recommendations could be transcribed, it is clear that the immediate objectives of Sulphlex research should be to:

1. Research the development of second generation Sulphlex binders that possess a lower Tg and less susceptibility to low temperature fracture or fracture due to rapid temperature drops.

2. Develop Sulphlex formulations that will retain the structural advantages of Sulphlex at midrange temperatures and that will achieve reasonable low temperature fracture resistance and resistance to stiffness degradation at combinations of high temperatures and very long durations of loading.

3. Improve the moisture and thermal aging durability of Sulphlex through the investigation of alternate chemical formulations and variations in process parameters.

4. Employ the fracture mechanics techniques discussed herein in the fracture characterization of second generation Sulphlex binders.

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