

# Chlorinated Polyolefins for Asphalt Binder Modification

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## SYNOPSIS

The benefits obtained from the addition of small quantities of chlorinated polyolefins to paving grade asphalt binders were investigated. A chlorinated polyethylene plastomer, Tyrin 2552, and a chlorinated olefinic elastomer, Tyrin CM0730, were added to asphalt binders at 3 and 5 wt % and subsequently reactively processed to facilitate compatibilization. The mixtures were analyzed for rheological performance relating to fatigue and rutting as well as low-temperature fracture performance. The addition of small quantities of these polymers to the asphalt binders resulted in significant improvements over conventional modifiers at both the high and low temperature extremes. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

In recent years pavement distress has increased significantly due to a substantial increase in automobile and truck traffic. In the United States, the Federal Highway Administration has reported a twofold increase in heavy truck traffic in the last 15 years alone.<sup>1</sup> Moreover, trucks are now allowed to use radial ply tires with internal air pressures as high as 110 psi compared to conventional bias ply tires that were pressurized at 85 psi.<sup>2</sup> It is the concomitant increase in distress that is causing a premature deterioration of our highway systems. Significant rutting and fracture of the asphalt pavement results in dangerous driving conditions. Drivers of small passenger cars easily lose control when crossing deep ruts, a problem only aggravated when water collects in the rutted areas resulting in a loss of wheel traction. For these reasons, local and federal governments have recently forced asphalt suppliers to produce better asphalt binders.

The purpose of this research was to investigate the benefits of adding several chlorinated polymers to asphalt binders for hot-mix paving applications. A chlorinated polyethylene and a chlorinated polyolefin elastomer were investigated for their poten-

tial in improving both low- and high-temperature performance of asphalt binders.

## BACKGROUND

Asphalt is a viscoelastic material; at high temperatures it is a viscous liquid, whereas at low temperatures it transforms into a brittle solid. This characteristic behavior allows us to mix asphalt at high temperatures with an aggregate and subsequently shape the mixture into a pavement. After the mixture cools to ambient temperatures, the asphalt binder holds the aggregate together and gives the pavement its unique elastic properties.

However, the viscous nature of the material also allows for permanent deformation, or rutting, to occur at service temperatures. During summer months, temperatures of pavement surfaces in North America can reach as high as 60 to 70°C. At this temperature, the asphalt loses its resilience and a single heavy truck can do as much rutting damage as 7000 automobiles.<sup>3</sup>

In the ambient temperature range of 5 to 35°C, a frequent occurrence resulting from repeated cyclic stresses of values less than the tensile strength of the pavement is fatigue cracking. Fatigue cracking is a serious problem in pavements subjected to high volumes of traffic. Fatigue resistance of a modified asphalt is very dependent on the type of polymer added: high strength elastomeric polymers have been reported to perform more favorably than plastomers.

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Some styrene-butadiene-styrene systems extend fatigue life 3 to 10 times.<sup>4</sup>

At the low temperature extreme, normal asphalt becomes too brittle to withstand significant thermal shrinkage during early winter months when large temperature changes can occur overnight. The brittle asphalt binder has no toughness, and small cracks, initiated by naturally occurring flaws in the pavement, can form large transverse cracks within a matter of weeks, due to recurring freeze-thaw cycles.

The idea of adding small quantities of polymer to asphalt binders is not new and has been demonstrated on numerous occasions.<sup>5</sup> A large number of polymers have been investigated for asphalt modification, most notably in Western Europe. Polyethylene,<sup>6,7</sup> random<sup>8</sup> and block<sup>9,10</sup> copolymers of styrene and butadiene, hydrogenated styrene butadiene block copolymers, ethylene vinyl acetate copolymers (EVA),<sup>11</sup> polypropylene,<sup>12</sup> neoprene,<sup>13</sup> and others have all been investigated as modifiers that improve the performance of asphalt binders. The advantages listed in the literature are quite numerous; most polymers claim to reduce temperature susceptibility resulting in less cracking at low temperatures and less rutting during summer months.

One problem often encountered when using polymer-modified asphalts is their lack of phase homogeneity. Due to the high molecular weight and rigid nature of the asphaltene fraction in the asphalt binder, high molecular weight synthetic polymers are usually not miscible in these systems. For polyethylene-modified binders it has often been reported that an initially homogeneous system quickly phase separates to form a thick congealed layer on top of the hot asphalt binder.<sup>14</sup> This problem has for a long time inhibited the large-scale acceptance of polyethylene modified asphalt binders.

Recently however, steric stabilizers have been developed to permanently prevent coalescence at typical storage temperatures for the binders.<sup>15</sup> Another solution to the incompatibility of polymers and asphalt has been employed by researchers in France. Styrene-butadiene rubbers were added to the asphalt in conjunction with small amounts of sulfur.<sup>16</sup> The sulfur both grafts asphalt onto the polymer backbone, thus making it soluble, and crosslinks the polymer to form a higher molecular weight modifier with better rheological properties.

We discuss a similar approach to obtain compatibility between polymer and asphalt. Chlorinated polymers were added to hot asphalt in conjunction with small amounts of Friedel-Crafts catalysts; in this case, anhydrous aluminum trichloride. The cat-

alyst was added in order to facilitate a reaction between the polymer and asphalt phase. The exact structure of asphalt varies from source to source and is not very well understood. However, in Figure 1 an illustrative structure for a Laquinillas petroleum asphaltene fraction is given.<sup>17</sup> The large number of aromatic alkyl substituents and allylic hydrogens in this asphalt molecule and in similar aromatic fractions in other asphalts, like those used in this work, should make the material in general quite amenable to both radical induced and electrophilic substitution reactions.

## EXPERIMENTAL MATERIALS

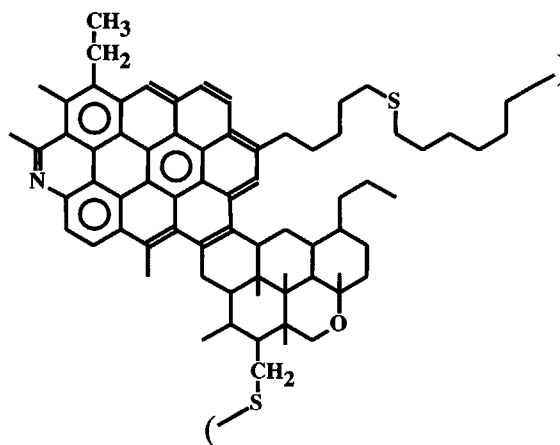
### Asphalts

Three different asphalts were used in this study. An 85–100 penetration grade and a 200–300 penetration grade asphalt were both obtained from the Esso Petroleum refinery in Montreal, Quebec. A 150–200 penetration grade asphalt was obtained from the Petro-Canada refinery in Clarkson, Ontario.

### Polymers

The chlorinated polymers used for modification of the asphalt binders were a plastomer, Tyrin 2552, and an elastomer, Tyrin CM0730, both from the Dow Chemical Company of Midland, MI. Their properties are given in Table I.

The fracture energies of a number of different conventional polymer modified asphalt binders were determined for comparison with the newly produced binders.



**Figure 1** Illustrative structure as proposed for a Laquinillas asphaltene fraction.<sup>17</sup>

**Table I Physical Properties of Tyrin 2552 and Tyrin CM0730**

Tyrin 2552	Chlorine content, %	25
	Molecular weight, g/mol	120,000
	Heat of fusion, cal/g	~ 12–14
	Residual crystallinity	~ 25%
	Specific gravity	1.10
Tyrin CM0730	Chlorine content, %	30
	Moony viscosity, ML <sub>1+4</sub> (121°C)	65
	Residual crystallinity, %	< 2
	Specific gravity	1.13

Recycled polyethylene stretch wrap was obtained from Du Pont Canada of Kingston, Ontario, and was added at 160°C under high shear to the asphalt binder just prior to being poured into the silicone mold to produce notched fracture beams. The stretch wrap had a fractional melt index and contained 1% polyisobutylene additive.

A ground rubber tire sample was obtained from Rouse Rubber Industries of Vicksburg, MS, and was dispersed under similar conditions as the polyethylene. The ground rubber was produced in a wet ambient grinding process and had an average particle size of 74 μm.

A commercial styrene-butadiene modified asphalt binder was obtained from Polymac Engineered Asphalts Corporation of Oshawa, Ontario. It contained 4% styrene-butadiene polymer which was *in situ* vulcanized and grafted in the asphalt binder to produce an 85–100 penetration grade asphalt. It had a penetration–viscosity number of 1.3 and a viscosity of 1.15 poises at 135°C.

### Catalyst

Anhydrous aluminum chloride, AlCl<sub>3</sub>, was obtained from Aldrich Chemical Co. and used as received.

## EXPERIMENTAL PROCEDURES

### Reactive Processing

Modification of the asphalt with the chlorinated polyolefins consisted of mixing the asphalt and polymer under high shear at 195°C for 4 h. Samples containing 3 and 5% chlorinated polymer were reacted with 0.3 and 0.5% AlCl<sub>3</sub>, respectively. Care was taken not to expose the catalyst to water because it would reduce its effectiveness. The recycled polyethylene and ground rubber tire mixtures were pre-

pared by dispersing the additive at 160°C for at least half an hour.

### Morphology

The phase structure of the modified asphalts was observed by heating a drop of asphalt between a glass slide and a cover slide to make a thin film, which was subsequently examined under a microscope at 400× magnification.

### Penetration–Viscosity Measurements

Penetration measurements were done according to ASTM standard D-5. The sample was placed under a needle that was loaded with a 100 g weight and was subsequently allowed to penetrate the sample for 5 s. The reported value is the depth of penetration measured in increments of 0.1 mm.

Viscosity measurements were made using a coaxial cylinder geometry in which the inner cylinder was rotating and the sample was maintained at a set temperature.

From the penetration and viscosity data, penetration indices and penetration–viscosity numbers were determined. The penetration index (PI) is calculated according to the following relationship:

$$PI = 20 - 500A/1 + 50A \quad (1)$$

where  $A$  is calculated according to:

$$A = \log(\text{Pen.}@T_1) - \log(\text{Pen.}@T_2)/T_1 - T_2 \quad (2)$$

In this work  $T_1 = 25^\circ\text{C}$  and  $T_2 = 15^\circ\text{C}$ .

The pen–vis number (PVN) is calculated using the following relationship:

$$PVN = -1.5(L - X)/(L - M) \quad (3)$$

where  $X$  is the viscosity measured in centistokes at 135°C, and  $L$  and  $M$  are calculated from the following formulae after McLeod:<sup>18</sup>

$$L = 4.25800 - 0.79670 \log(\text{Pen}) \quad (4)$$

$$M = 3.46289 - 0.61094 \log(\text{Pen}) \quad (5)$$

where  $\text{Pen}$  is the penetration measured at 25°C.

Both the penetration index and the penetration–viscosity number are widely used empirical parameters in the asphalt industry to indicate the temperature sensitivity of a particular asphalt binder. A low-temperature susceptible asphalt will have a

reasonable flexibility at low service temperatures and a reasonably high viscosity at high service temperatures. Most unmodified paving grade asphalts have a PI between  $-1$  and  $1$ . Those with a PI of less than  $-2$  are highly temperature susceptible and often fail at both temperature extremes, i.e., are too brittle at low temperatures and too soft at high temperatures. Unmodified asphalts have a typical PVN between  $-2$  and  $0.5$ , whereas polymer-modified asphalts can have a PVN anywhere over  $0.3$ . The higher this number, the more favorable the temperature response of the asphalt binder.

### Dynamic Mechanical Testing

Samples were heated until liquid, usually in the range of  $130$ – $140^\circ\text{C}$ , poured into a combined melts and solids (CMS) test fixture, and allowed to cool to room temperature. The sample was then smoothed flat using a hot metal scraper, and allowed to cool again. No pretest conditioning of the sample was employed.

Testing was done with a Rheometrics Dynamic Analyzer RDA II equipped with a liquid nitrogen supply to maintain low temperature conditions. The CMS fixture consists of a  $42$  mm diameter cup and a bilevel plate that has an  $8$  mm diameter serrated surface concentric with and projecting from a  $25$  mm diameter plate. Data for the solid and the melt is obtained from the same sample by using the  $8$  mm surface of the plate below  $40^\circ\text{C}$  and the  $25$  mm surface above this temperature. Curves for  $|G^*| \sin \delta$  and  $|G^*|/\sin \delta$  were generated using programmed temperature sweeps at  $10$  rad/s in the temperature range of interest.

All data is calculated automatically by the RDA II software using the input strain  $\gamma$  and strain angle, and the measured stress  $\tau$  and stress angle.<sup>19</sup>

### Fracture Mechanics

Sample preparation for low-temperature testing involved pouring hot liquid asphalt into a notched silicone rubber mold that was then cooled in a freezer for at least  $12$  h. The samples were tested using a three-point bending test based on ASTM method D-790. Testing was done in a liquid nitrogen-cooled temperature chamber, maintained at  $-20^\circ\text{C}$ , using a computer interfaced Sintech 2/G testing frame. The sample bars measured  $25$  mm wide by  $12.5$  mm deep by  $175$  mm long, and had a  $90^\circ$  starter notch  $5$  mm deep in their center that was sharpened with a razor blade just prior to testing. The length of the loading span was  $100$  mm.

A common assumption to avoid the difficulties presented by viscoelasticity in the study of a viscoelastic composite material, especially at low strain rates, is to assume that the composite adheres to the theory of linear elasticity. This is a valid assumption when the moduli of the matrix and the added polymer phase vary only slightly with time; however, the approximation is not justified when either of the two components is near its glass transition. Because typical paving grade asphalts have a glass transition around  $0^\circ\text{C}$ <sup>20</sup> and the fracture tests are all performed at  $-20^\circ\text{C}$ , the assumption of linear elasticity is not unreasonable.

Linear elastic fracture mechanics (LEFM) utilizes two main parameters: the critical stress intensity factor or fracture toughness  $K_{Ic}$ , and the fracture energy  $G_{Ic}$ . Samples must be provided with a starter notch to ensure that cracking occurs in the right place. To ensure that plane-strain conditions exist at the crack tip it is necessary that the thickness be large with respect to the plastic zone size; otherwise, plane-stress conditions will develop.

Brittle fracture studies were completed for 10 different samples, including the base asphalts, asphalt-polymer mixtures, and three conventional polymer-modified asphalt binders. Measured data included the failure load and the modulus, from which the fracture toughness and the fracture energy were calculated according to Eqs. (10) and (11) below.<sup>21,22</sup>

$$K_{Ic} = \frac{P_f S}{B W^{3/2}} \times \frac{3 \left( \frac{a}{W} \right)^{1/2} \left[ 1.99 - \frac{a}{W} \left( 1 - \frac{a}{W} \right) \times \left( 2.15 - 3.93 \frac{a}{W} + 2.7 \frac{a^2}{W^2} \right) \right]}{2 \left( 1 + 2 \frac{a}{W} \right) \left( 1 - \frac{a}{W} \right)^{3/2}} \quad (10)$$

$$G_{Ic} = \frac{K_{Ic}^2}{E} (1 - \nu^2) \quad (11)$$

Where;

- $K_{Ic}$  = fracture toughness,  $N \text{ m}^{-3/2}$
- $G_{Ic}$  = critical fracture energy,  $J \text{ m}^{-2}$
- $P_f$  = applied failure load,  $N$
- $S$  = loading span,  $m$
- $B$  = specimen depth,  $m$
- $W$  = specimen width,  $m$
- $a$  = crack length,  $m$
- $E$  = Young's Modulus,  $N \text{ m}^{-2}$
- $\nu$  = Poisson's ratio.

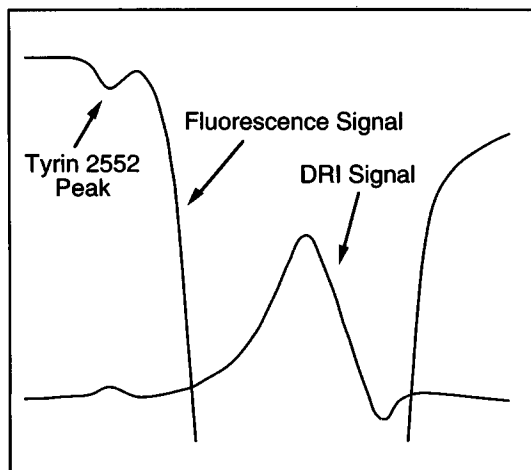
It may be useful to investigate the fracture behavior of the binders at different temperatures, in which case the critical strain energy release rate,  $J_{Ic}$  from the theory of elastic-plastic fracture mechanics (EPFM) may be a more appropriate indicator for fracture resistance.<sup>23</sup>

## RESULTS AND DISCUSSION

### Morphology

It was found that reactive processing had rendered the 3% and 5% Tyrin 2552 marginally soluble in the asphalt phase, i.e., no phase separation was observed at 400 $\times$  magnification of a freshly reacted sample. However, heating a thin film of the mixture resulted in slow phase separation of the polymer. The 3% additive showed a few stable particles of approximately 1  $\mu\text{m}$  in diameter and the 5% polymer additive showed a few particles of approximately 3  $\mu\text{m}$  in diameter. However, no gross phase separation as it occurs in regular polyethylene-asphalt systems was observed.

The reacted mixture was dissolved in THF and filtered for gel permeation chromatographic analysis of which the results are given in Figure 2. From the curves it can be concluded that there has been some reaction between the asphalt and the chlorinated polymer because the fluorescence signal shows a distinct peak at approximately 150,000 g/mol (polystyrene equivalent) molecular weight. This is in contrast to the results for an unmodified binder that did not show any such peak in the chromatogram.



**Figure 2** Gel permeation chromatography results for reactively processed 5% Tyrin 2552 in a 200–300 penetration grade asphalt.

The mixture containing 3% Tyrin CM0730 had some gelled particles that were irregular in shape, ranging in size from less than 10  $\mu\text{m}$  to as large as 150  $\mu\text{m}$ , indicating the slightly crosslinked structure of the polymer.

The 5% ground rubber tire particles were irregularly shaped and ranged in size from 5 to 150  $\mu\text{m}$ . The recycled polyethylene modified binder showed round particles ranging in size from 3 to 10  $\mu\text{m}$ . The morphology of the two latter materials is given in Figure 3.

### Penetration-Viscosity Testing

Values of the penetration at 25°C, the viscosity at 135°C, the penetration index (PI) and the pen-vis number (PVN) for the different polymer modified binders are summarized in Table II.

It should be realized that these data are only very rough indicators for the rheological performance of these binders in an actual hot-mix pavement. To obtain a more accurate correlation with pavement performance, dynamic mechanical rheological data for the binders are needed.<sup>24</sup>

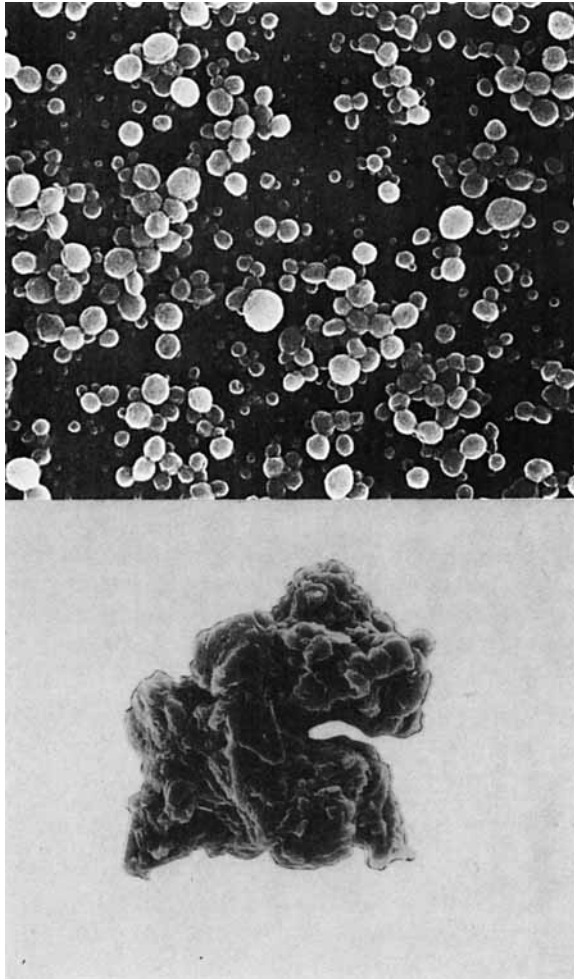
### Dynamic Mechanical Testing

An elegant and more informative method of rheological testing is to subject a material to an oscillatory strain and measure the subsequent stress that the sample experiences.

The recently completed United States' Strategic Highway Research Program (SHRP) has designed an Asphalt Binder Specification requiring minimum or maximum values for parameters relating to three forms of pavement distress. The three failure modes are low-temperature cracking, fatigue cracking, and permanent deformation, the latter two measurable by dynamic testing. The parameters used to describe fatigue cracking and permanent deformation due to rutting are  $G^* \sin \delta$  and  $G^* / \sin \delta$ . In order to conform to one of the specification grades listed in Table III,  $G^* / \sin \delta$  is required to have a minimum value of 1.0 kPa at the corresponding test temperatures.

From Figure 4 it is seen that the 200/300 sample reaches the 1 kPa minimum at 54°C, while the 150/200 and 85/100 penetration grades reach the 1 kPa level at 57 and 64°C, respectively. The SBR sample conforms to a PG 68 grading while the 5% CM0730 and the 4% stabilized recycled polyethylene reach the 1 kPa level at 84 and 86°C, respectively.

The 5% Tyrin 2552 sample has the best high temperature performance because it only reaches the 1 kPa minimum requirement at 116°C. In the actual pavement it is, therefore, anticipated that the poly-



**Figure 3** Particle morphology for recycled polyethylene stretch wrap and ground rubber tire modifiers.

mer-modified asphalts perform much better than the unmodified binders. The Tyrin 2552-modified binder should perform satisfactorily up to temperatures of 116°C. The reason for this large increase in high temperature properties is thought to arise from the

high compatibility and high molecular weight of the chlorinated polyethylene.

Figures 5 and 6 show the fatigue resistance parameter,  $G^* \sin \delta$ , for unmodified and modified asphalt binders, respectively. It has been proposed by the Strategic Highway Research Program that at the average pavement temperature an aged asphalt binder should have a maximum value of 5,000 kPa for this parameter. Values beyond the 5,000 kPa limit will render a pavement susceptible to fatigue cracking. From Figure 6 it is obvious that none of the modifiers change the fatigue susceptibility of the base asphalts to any significant extent.

It remains to be investigated in field trials if the improvements in the parameter for rutting resistance of the binder does, indeed, translate into improved performance of the pavement. However, validation is beyond the scope of this research. At this point we only want to show the very significant differences between the chlorinated polymers and conventional modifiers.

#### Low-Temperature Fracture Tests

The Strategic Highway Research Program binder specifications use direct tension and creep stiffness tests on aged binder residues as a means of determining low-temperature performance. However, the bending beam test is not realistic for examining the effectiveness of polymer modifiers because the addition of 5% polymer will, by the rule of mixtures, not have any appreciable effect on the binder stiffness. On the other hand, 5% polymer will have a tremendous effect on the value of the failure strain. The authors feel that the fracture toughness,  $K_{Ic}$ , of the unaged binder is a more meaningful parameter because it actually determines a material property of the asphalt binder under controlled conditions of temperature and stress field.

During testing it was observed that a small num-

**Table II** Penetration-Viscosity Data

Asphalt	Polymer	Pen [dmm]	Viscosity [cP]	PI	PVN
200-300	—	189.0	65	+1.98	-2.54
200-300	3% 2552	65.0	1100	+4.60	+0.74
200-300	5% 2552	52.5	3700	+4.96	+2.94
200-300	3% CM0730	75.0	1100	+3.73	+0.93
200-300	5% CM0730	72.0	1900	+2.99	+1.67
Styrelf	4% SBR	90.8	1150	+1.20	+1.31
150-200	5% GRT	104	—	+1.25	—

**Table III SHRP Asphalt Binder Specifications for Rutting Resistance**

Performance Grade	PG 52	PG 58	PG 64	PG 70
Average 7-day maximum pavement design temperature, °C	< 52	< 58	< 64	< 70
$G^*/\sin \delta = 1$ kPa minimum @ test temperature, °C	52	58	64	70

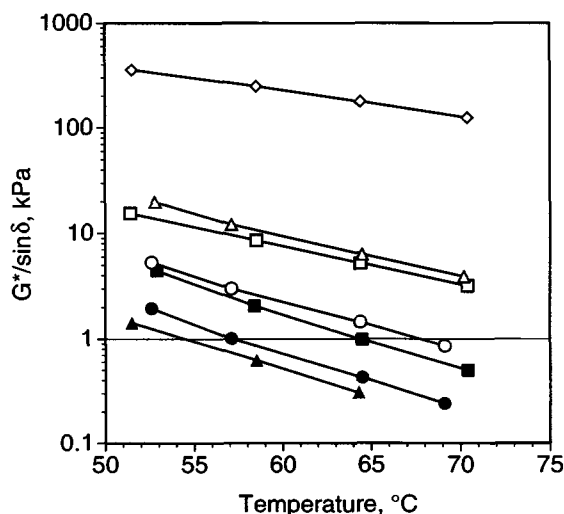
ber of test pieces (< 5%) were not breaking in a brittle fashion, but were yielding at an applied load value around that at which the sample was normally expected to fail. These test beams were able to sustain significantly higher loads but did eventually fracture. The mixtures for which this phenomenon was observed to occur were unmodified 200–300, 3 and 5% Tyrin 2552, 5% Tyrin CM0730, and 5% ground rubber tire. Test pieces that yielded were not included in the calculations of  $K_{Ic}$  and  $G_{Ic}$ .

In the calculation of  $G_{Ic}$  the term involving Poisson’s ratio has been omitted because it was not determined and only has a minor quantitative influence on the calculated result. For each binder a minimum of 10 beams were fractured, and from the data, the average failure loads and standard deviations were calculated. The fracture toughness and fracture energy were calculated from the failure load, the bending beam modulus, and the beam dimensions. Typical force–displacement curves for the tested

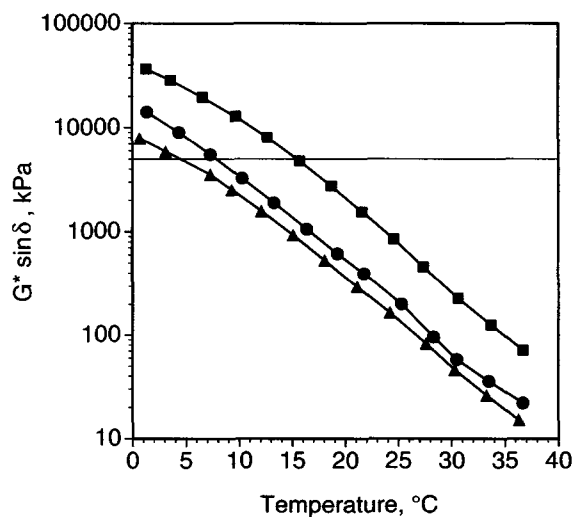
samples are given in Figures 7–9. As seen from these curves, fracture occurs in a brittle fashion and the application of linear–elastic fracture mechanics does not seem unreasonable. The fracture toughness and fracture energy data calculated from the failure stresses and bending beam moduli are summarized in Table IV.

The pure 85–100 and 200–300 penetration grade binders have fracture energies of 1.5 and 6.0 J m<sup>-2</sup>, respectively. These values are indicative of brittle failure of a low molecular weight elastic solid. A single crack is initiated at the notch and can grow unimpeded until catastrophic failure occurs without the consumption of a significant amount of energy.

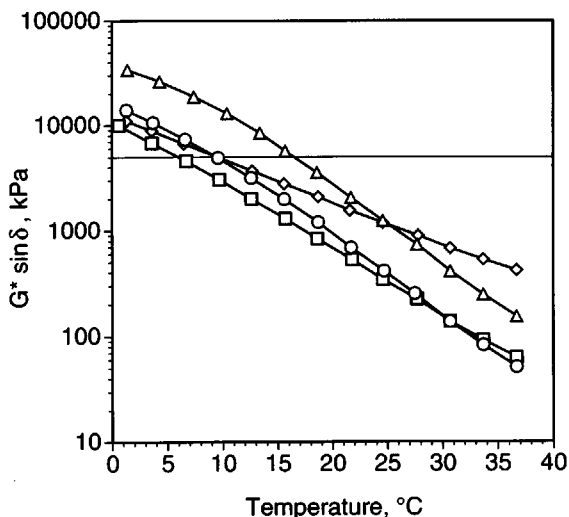
From the data in Table IV it is clear that as an additive the Tyrin 2552 plastomer outperforms all other modifiers. The reason for this may be explained by the different morphology of this modified binder. The Tyrin 2552 is almost dissolved in the asphalt phase where it can prevent brittle failure due to its high molecular weight. It facilitates some kind of plastic deformation mechanism at the crack



**Figure 4** Rutting resistance parameter,  $G^*/\sin \delta$ , for different binders (▲—200/300 grade, ●—150/200 grade, ■—85/100 grade, ○—4% SBR modifier, □—5% Tyrin CM0730 modifier, △—4% PE modifier, and ◇—5% Tyrin 2552 modifier).



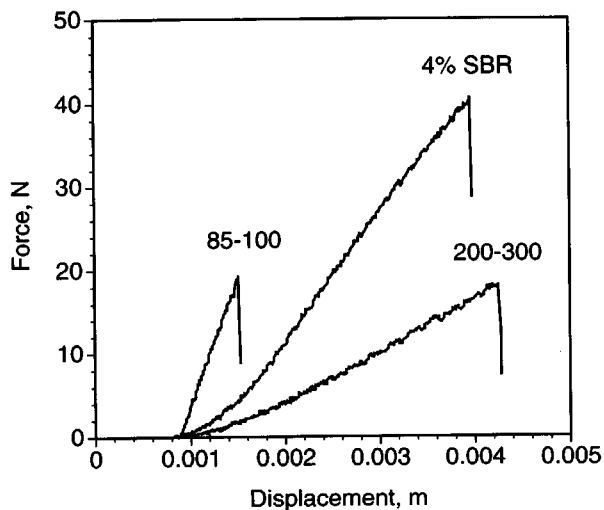
**Figure 5** Fatigue resistance parameter,  $G^* \sin \delta$ , for unaged binders (▲—200/300 grade, ●—150/200 grade, ■—85/100 grade binder).



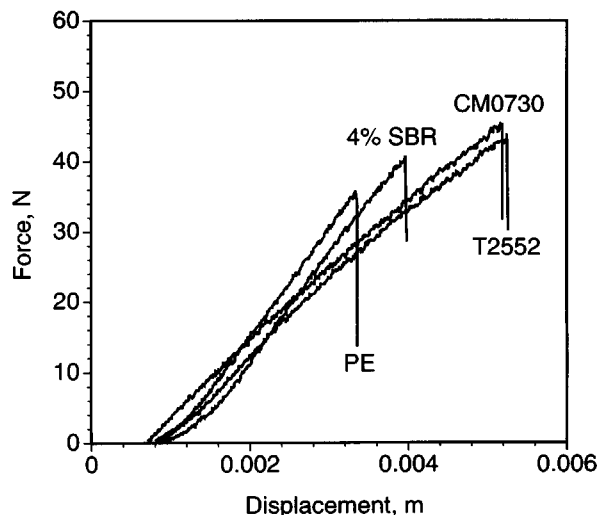
**Figure 6** Fatigue resistance parameter,  $G^* \sin \delta$ , for unaged binders ( $\square$ —4% SBR modified,  $\circ$ —5% Tyrin CM0730 modified,  $\triangle$ —4% PE modified, and  $\diamond$ —5% Tyrin 2552 modified binder).

tip when the sample is loaded. Failure in this particular binder occurs at much higher stress levels than for other modified or unmodified binders.

At this moment the desire to understand the exact reason for this significant increase provides a basis for further research. When toughening brittle thermoplastics, often two basic mechanisms, crazing and shear yielding, are promoted to increase fracture resistance. It is the subject of current research to determine which mechanisms cause the increase in toughness seen with the addition of polymers to an asphalt binder.<sup>25</sup>



**Figure 7** Force-displacement curves for control samples ( $-20^\circ\text{C}$  and  $0.01 \text{ mm/s}$  loading rate).

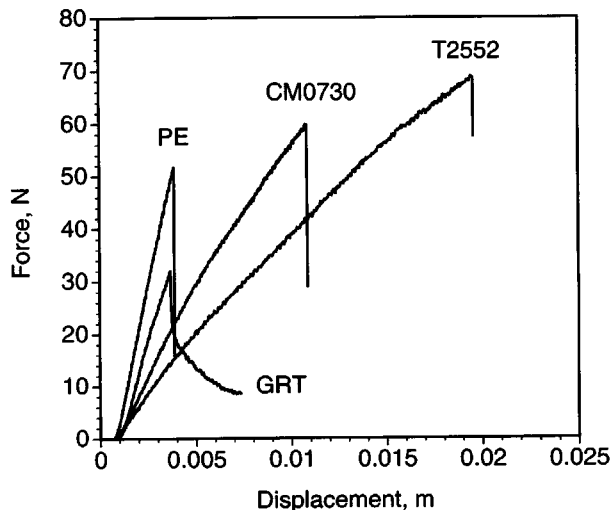


**Figure 8** Force-displacement curves for polymer-modified asphalt binders (3% additive,  $T = -20^\circ\text{C}$  and  $0.01 \text{ mm/s}$  loading rate).

### CONCLUSIONS

In this work two new asphalt additives were investigated for both high-temperature rheological behavior and low-temperature fracture behavior. The properties of these modified binders were compared with those of conventionally modified binders.

It should be emphasized that the comparisons between different polymer modifiers in this study were made on an equal weight percent basis for the additive. This may not be the most suitable comparison because it will eventually be the cost/per-



**Figure 9** Force-displacement curves for modified asphalt binders (5% additive,  $T = -20^\circ\text{C}$  and  $0.01 \text{ mm/s}$  loading rate).



**Table IV Low Temperature Fracture Data on Polymer Modified Binders**

Asphalt	Polymer	Modulus [GPa]	$K_{Ic}$ [kJ m <sup>-1.5</sup> ]	$G_{Ic}$ [J m <sup>-2</sup> ]
85-100	—	1.4 ± 0.1	44.1 ± 3.9	1.5 ± 0.3
200-300	—	0.45 ± 0.03	50.4 ± 2.9	6.0 ± 0.9
200-300	3% 2552	0.50 ± 0.08	103.0 ± 20.4	26.6 ± 12.8
200-300	3% CM0730	0.54 ± 0.03	101.2 ± 7.6	19.9 ± 3.5
150-200	3% XPE	0.75 ± 0.04	78.8 ± 4.1	8.5 ± 1.1
200-300	5% 2552	0.42 ± 0.03	154.5 ± 7.6	57.6 ± 7.0
200-300	5% CM0730	0.35 ± 0.07	133.8 ± 12.0	45.4 ± 8.2
150-200	5% GRT	0.57 ± 0.04	73.3 ± 4.1	10.0 ± 1.69
150-200	5% XPE	0.66 ± 0.06	110.9 ± 4.7	19.2 ± 2.0
Styrelf	4% SBR	0.71 ± 0.03	86.1 ± 8.8	12.2 ± 2.6

Values are given with 90% confidence interval.

formance ratio that will be the determining factor deciding which additive will be most desirable for application in a pavement.

Both the chlorinated plastomer and elastomer showed improved compatibility with the asphalt binders after reactive processing at elevated temperatures. This improved compatibility resulted in a significant increase of both the penetration index and penetration-viscosity number over an unmodified binder. This is not an unexpected phenomenon and has regularly been demonstrated in other studies on polymer-modified asphalt binders.<sup>10,26</sup> At only 3% additive to the binder, the penetration-viscosity number is increased from -2.54 to +0.74. This significant improvement will result in enhanced rheological performance for the pavement during hot summer months while the binder will also be able to withstand cold winter temperatures.

Dynamic mechanical tests confirmed the penetration results, and demonstrated the effect that the polymer modifiers, especially Tyrin 2552, had on the rutting resistance parameter,  $G^*/\sin \delta$ , for the modified binders.

More interesting results were obtained with the low-temperature fracture studies on the control and modified binders. If polymers are added to asphalt binders, substantial increases in fracture energy are observed. For samples containing only 5% chlorinated polyethylene, the fracture energy determined was as high as 57.6 J m<sup>-2</sup>. Compared to an unmodified 85-100 grade asphalt, this is an almost 40-fold increase.

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## REFERENCES

1. B. Eckmann, *Proc. Assoc. Asphalt Paving Technol.*, **58**, 337-361 (1989).
2. P. Joseph, J. H. Dickson, and G. Kennepohl, *Can. Tech. Asphalt Assoc. Proc.*, **37**, 243-269 (1992).
3. J. J. Emery and T. H. Johnston, *Can. Tech. Asphalt Assoc. Proc.*, **32**, 340-351 (1987).
4. G. King, H. Muncy, and J. Prudhomme, *Proc. Assoc. Asphalt Paving Tech.*, **55**, 519-540 (1986).
5. K. R. Wardlaw and S. Shuler, Eds., *Polymer Modified Asphalt Binders*, American Society for Testing and Materials, Special Technical Publication 1108, 1992.
6. S. A. M. Hesp and R. T. Woodhams, in *Polymer Modified Asphalt Binders*, K. R. Wardlaw and S. Shuler, Eds., ASTM STP. 1108, 1-19, 1992.
7. S. A. M. Hesp, Z. Liang, and R. T. Woodhams, U.S. Pat. No. 5,280,064 (1994).
8. S. L. Cumbaa and H. R. Paul, in *Report FHWA/LA-88/211*, Louisiana Transportation Research Center, Louisiana Department of Transportation and Development, 1988.
9. N. Predoehl, in *Modified Asphalt Binders for Stability Improvement*, Construction Evaluation Report, Office of Transportation Laboratory, California Department of Transportation, 1988.
10. W. C. Vonk and A. L. Bull, in *Thermoplastic Rubbers Technical Manual TR 8.17*, Shell Elastomers, 1989.
11. R. D. Ramsay, U.S. Pat. No. 3869417 (1975).
12. R. Reese, in *Evaluation of Three Types of Fiber and Carbon Black as an AC Additive To Resist Abrasion: Construction Report*, Office of Transportation Laboratory, California Department of Transportation, 1986.
13. J. W. Button, *Transport. Res. Rec.*, **1342**, 67-75 (1992).
14. S. A. M. Hesp and R. T. Woodhams, *Colloid Polym. Sci.*, **269**, 825-834 (1991).
15. Z. Liang and S. A. M. Hesp, *Colloids Surf., A*, **81**, 239-250 (1993).

16. J. P. Planche, F. Travers, and A. Zins, PCT WO 90/02776, 1990.
17. T. F. Yen, in *Chemistry of Asphaltenes*, Am. Chem. Soc., Adv. Chem. Ser. 195, J. W. Bunger and N. C. Li, Eds., Washington, DC, 1979, p. 39.
18. N. W. McLeod, *J. Test. Evaluat.*, **4**(4), 275 (1976).
19. Owners Manual, Rheometrics Dynamic Analyzer RDA II, pp. 8-19-8-21, Rheometrics, Inc., 1990.
20. P. Claudy, J. M. Letoffe, G. N. King, and J. P. Planche, in *Proceedings, International Symposium, Chemistry of Bitumens*, Vol II, C. Giavarini and J. G. Speight, Eds., Rome, Italy, 1991, pp. 530-567.
21. D. Broek, *Elementary Engineering Fracture Mechanics*, 3rd. revised ed., Martinus Nijhoff, The Hague, 1982, p. 171.
22. A. J. Kinloch and R. J. Young, *Fracture Behaviour of Polymers*, Elsevier Applied Science, New York, 1983, p. 93.
23. R. Dongre, M. G. Sharma, and D. A. Anderson, *Transport. Res. Rec.*, **1228**, 94-105 (1989).
24. G. N. King, H. W. King, O. Harders, P. Chavenot, and J. P. Planche, *Proc. Assoc. Asphalt Paving Technol.*, **61**, 29-66 (1992).
25. N. K. Lee and S. A. M. Hesp, *Transport. Res. Rec.*, 1994 (to appear).
26. C. P. Valkering, D. J. L. Lancon, E. de Hilster, and D. A. Stoker, *Proc. Assoc. Asphalt Paving Technol.*, **59**, 590-609 (1990).

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