

# Modification of Asphalt Binders and Asphalt Concrete Mixes with Crumb and Chemically Devulcanized Waste Rubber

GEOFFREY R. MORRISON, ROB VAN DER STEL, AND SIMON A.M. HESP

For this study of the modification of asphalt binders with crumb and devulcanized waste rubber, rubber digestion aids were investigated for their ability to devulcanize waste tire crumbs. It was found that none of the commercially available chemical agents were able to totally devulcanize the crumb rubber. However, high yields of devulcanization were obtained with chlorothiophenols. The devulcanized and crumb rubbers were added to asphalt binders, and their low temperature performance was studied. It was found that the fracture toughness of the devulcanized rubber system was higher than that for both the control asphalts and a commercially available oxidized rubber system. Toughening is mainly due to crack pinning and shear yielding mechanisms for crumb rubber systems. However, only enhanced shear yielding mechanisms are responsible for the increase in toughness found in devulcanized rubber systems. Further work on the asphalt-aggregate mix should tell us if the improved performance of devulcanized binder systems will give enhanced pavement performance.

The development of rubber modified pavements has been a concern of highway materials engineers for nearly 30 years. The initial objective of research in this area was to improve the low and high temperature performance of roads. More recently, however, the focus has shifted due to environmental and political concerns about the growing scrap tire disposal problem. This has ultimately led to Section 1038 of the Intermodal Surface Transportation Efficiency Act (ISTEA) of 1991, which requires the use of scrap rubber tire in federally funded highway projects starting in 1995 (1).

## BACKGROUND

### Crumb Rubber Systems

C.H. McDonald, a materials engineer for the city of Phoenix, Arizona, developed the idea to use waste rubber as a modifier for asphalt binders in 1966. Since then, several variations of the original process have been widely used. The two main methods of modification are the dry process and the wet process. Each has certain limitations and advantages (2-4).

The dry process uses crumb rubber as part of the aggregate in a hot mix pavement. This process uses about 0.5 to 5 percent by weight of the aggregate of crumb rubber as small as 30 mesh, which usually fills a gap in the aggregate gradation. Results from Alaska and Sweden have suggested the use of different aggregate gradation bands depending on traffic volume. No special equipment is required for this process but it is limited to hot mix applications.

The wet process is a procedure in which 18 to 26 wt percent ground rubber tire, usually in the range of 8 to 20 mesh, is added to the asphalt binder and mixed at elevated temperatures (175°C to 220°C) for 1 to 2 hr. The rubber particles become swollen in the asphalt's oily phase forming a gel, to which some aromatic oil is often added to aid in processing. This process requires at least 20 percent more asphalt than a normal hot mix, which may be the main reason these pavements can show improved properties. The higher cost of the wet process has limited its use to stress absorbing membranes, to crack and joint sealing, and to a lesser extent to thin asphalt concrete overlays.

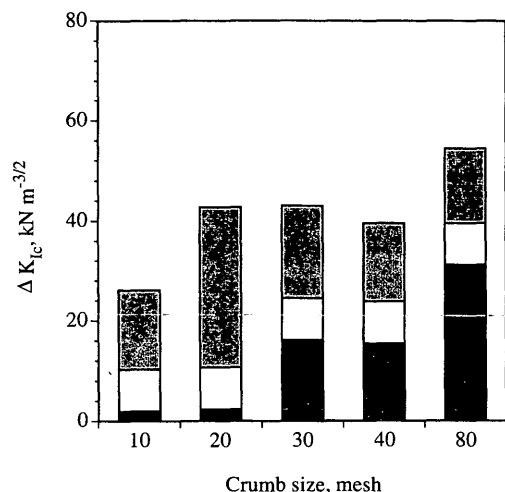
Rouse Rubber Industries has recently developed a process using very fine 80 mesh crumb rubber particles, for which they claim a much smaller cost increase than for both the conventional wet and dry processes (5). This process has recently been used in paving trials in both Ontario (6) and Florida (7). At present it is too early to comment about the performance of these test sections.

An extension of the wet process, by way of reactive compatibilization of the asphalt-crumb rubber interface, has shown that small amounts of crumb rubber reacted with a coupling agent can give low temperature fracture performance as well as, or better than, more costly binders with a high rubber loading (8). The added effect on the low temperature fracture toughness of interfacial grafting a low molecular weight polybutadiene onto the crumb rubber is shown in Figure 1.

### Devulcanized Systems

By devulcanizing rubber waste in asphalt, a homogeneous binder may be produced that can be stored at high temperatures for prolonged periods of time without the complications associated with slow sedimentation of the rubber that occurs when crumbs are added.

The idea of adding waste rubber that will dissolve in the asphalt to produce a homogeneous single phase system was first patented by Scott in 1972 (9). The process involved oxidative degradation of rubber in a liquid hydrocarbon that was then added to the asphalt binder. Similar patents that use solvent oils and soluble rubbers to produce gel-like compositions in which the crumb rubber is swollen with oil were assigned to Winters and McDonald (10), and Nielsen and Bagley (11). Subsequent inventions use blends of elastomeric rubbers and crumb rubber in asphalt (12,13). It is important to note that unless specific devulcanization agents or very high temperatures and long devulcanization times are used, as in Scott's 1972 invention, the crumb rubber particles will only swell in the added oils. Recently, Liang and Woodhams (14) have used a similar approach to that of Scott. They also add the crumb rubber to a hot aromatic oil and subsequently shear it until the rubber dissolves; the oil-rubber mixture is then diluted with asphalt.



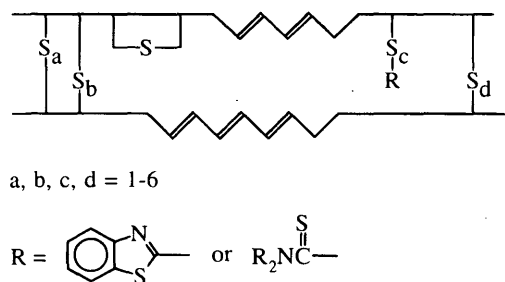
(Black—effect of crumb rubber, white—effect of additive and grey—effect of interfacial modification)

**FIGURE 1** Effect of interfacial modification on the low temperature fracture toughness of crumb rubber modified asphalt binder (8).

In general, devulcanization of rubber may be accomplished by using either an oxidative or a reductive path. The cross-linked molecular structure of a typical rubber is shown schematically in Figure 2 (15). The relative distribution of sulfur among the various structures will depend on the structure of the rubber, the temperature at which vulcanization took place, the composition of the vulcanization mixture, and the age of the rubber tire. High vulcanization accelerator concentrations tend to lead to more monosulfide cross-links and pendant accelerator complexes, whereas high temperature and old age tend to lead to more backbiting with an accompanying loss of functionality. In recycled rubber tire, however, it is reasonable to assume that most sulfur remains in polysulfide linkages.

#### Oxidative Devulcanization

Oxidation of disulfide linkages may be accomplished by reaction with peroxides or peracids, singlet oxygen, and by ozonolysis. A general mechanistic scheme for these oxidation reactions is shown in Figure 3 (16). Obviously, the oxidation of sulfur linkages is a complex



**FIGURE 2** Illustrative structure for cross-linked rubber (15).

process, and a number of products can be formed. Moreover, the oxidative agents used can also attack the SBR polymer backbone, eventually reducing the molecular weight of the devulcanized rubber.

Following the approaches taken by Schmidt et al. (17), Biegenzein (18), and Hoeher et al. (19) for the compatibilization of polymers in asphalt, Duong and Boisvert (20) have recently developed a process for the oxidative devulcanization of crumb rubber in asphalt binders. The procedure involves air blowing under pressure a mixture of crumb rubber and asphalt between 220°C and 260°C. The rubber is devulcanized by an electrophilic oxidation reaction with singlet oxygen, which cleaves sulfur-sulfur bonds to give a sulfonic acid (see Figure 3).

However, it is well known that air blowing of asphalt at temperatures well above 200°C may result in the oxidation of the asphalt itself, producing a harder and more brittle binder with poor low temperature and long-term fatigue performance (21). All oxidative methods of in situ rubber devulcanization are rather undesirable because of the associated oxidative degradation of the asphalt.

#### Reductive Devulcanization

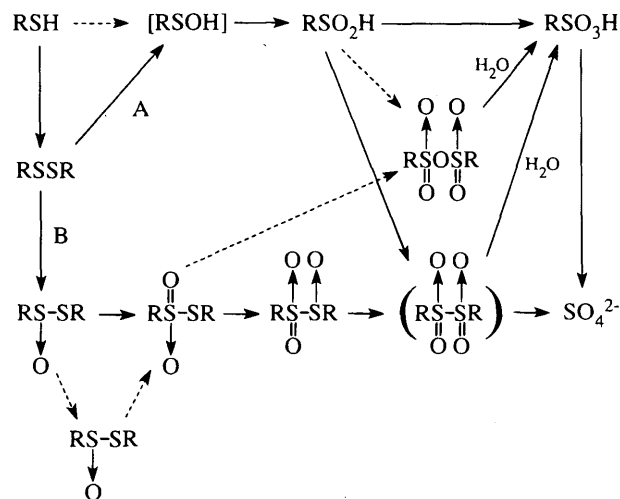
Reduction of disulfides to thiols by homolytic cleavage results from heating in the presence of reducing agents such as tetralin, decalin, secondary amines, or chlorothiophenols. Three examples for the reductive cleavage of sulfide linkages are given in Figure 4 (16). The thiols formed can subsequently be oxidized and react with labile groups within the asphalt resulting in an asphalt graft onto the rubber molecule.

In this study a number of oxidizing and reducing agents have been investigated for their efficiency in devulcanizing crumb rubber systems in a high boiling solvent (1,2,4-trichlorobenzene). The devulcanized rubber was subsequently added to asphalt to investigate the low and high temperature performance of the binders.

## EXPERIMENTAL PROCEDURES

### Materials

The 1,2,4-trichlorobenzene used for the devulcanization of crumb rubber, the tetrahydrofuran used in the gel permeation chromatography,

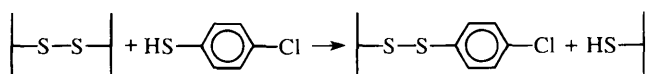


**FIGURE 3** General disulfide oxidation scheme (16).

## Secondary Amines:



## 4-Chlorothiophenol:



## 1,2,3,4-Tetrahydronaphthalene:

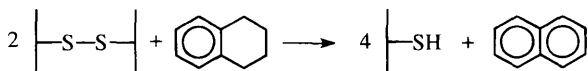


FIGURE 4 Reductive pathways for the devulcanization of cross-linked rubber (16).

graph, and the 4-chlorothiophenol were obtained from the Aldrich Chemical Company of Milwaukee, Wisconsin.

The Leegen 6130 devulcanization aid contained approximately 50 percent sulfonated petroleum products and was obtained from R.T. Vanderbilt of Norwalk, Connecticut. The Renacit 7 devulcanization aid contained approximately 50 percent pentachlorothiophenol as the active agent and was obtained from Miles of Akron, Ohio. The Plastone devulcanization aid contained a complex mixture of fatty acids, rosin acids, and isopropanolamines and was obtained from Harwick of Akron, Ohio. The MOTS 1 devulcanization aid contained between 45 and 55 wt percent thiuram disulfide as the active agent and was obtained from the American Cyanamid Company of Wayne, New Jersey.

The cryogenically ground rubber tire was obtained from Recovery Technologies of Mississauga, Ontario. The binder containing 10 wt percent oxidatively devulcanized rubber was obtained from Bitumar of Montreal, Quebec. The liquid polybutadiene, Ricon R-134, was obtained from Ricon Resins of Grand Junction, Colorado. The elemental sulfur used for the interfacial modification of the crumb rubber-asphalt systems was obtained from the Aldrich Chemical Company.

The 85-100 and 150-200 penetration grade asphalts were obtained from the Oakville, Ontario, refinery of Petro-Canada. Both binders were prepared from Bow River crude.

### Devulcanization of Crumb Rubber

Devulcanization of crumb rubber was carried out by refluxing the rubber crumbs in an organic solvent at high temperature in the presence of a chemical devulcanizing agent. In a typical reaction, 300 ml of 1,2,4-trichlorobenzene (boiling point 214°C) containing 20 grams of No. 10 mesh cryogenically ground rubber and 10 percent devulcanizing agent by weight of the rubber were charged to a 1000 mL roundbottom flask and refluxed with stirring for 2 hr. After cooling, the mixture was filtered through a 100 mesh stainless steel screen and the residue dried under 28 in. of mercury vacuum at 50°C for at least 8 hr. The mass of the dry residue on the screen was subtracted from the original mass of the rubber to determine the yield of the reaction. The effectiveness of several different devulcanizing agents was examined.

Devulcanized rubber was recovered by removing most of the trichlorobenzene in a rotary evaporator under vacuum, and then removing any remaining solvent in a vacuum oven under standard conditions. Molecular weight analysis of the devulcanized rubber was conducted using a Waters Associates gel permeation chromatograph with tetrahydrofuran as the eluent solvent.

### Binder Preparation

Crumb rubber modified binders were prepared by adding 10 wt percent 20 mesh cryogenic ground car tire and 2 wt percent Ricon R-134 liquid polybutadiene (LPBD) of molecular weight 12,000 g mole<sup>-1</sup> to a 150-200 penetration grade asphalt. A surface compatibilization reaction was facilitated by adding a further 1 wt percent sulfur to one of the crumb rubber/LPBD-asphalt mixtures. Samples with and without sulfur were mixed for 2 hr at 150°C to 170°C by using a high shear Polytron mixer manufactured by Brinkmann Industries of Mississauga, Ontario.

The devulcanized rubber modified binders were made by adding 10 wt percent devulcanized rubber, obtained from the chemical devulcanization studies, under high shear mixing to a 150-200 penetration grade asphalt.

### Asphalt Binder Tests

#### Dynamic Mechanical Testing

Samples were heated until liquid at 130°C to 140°C, poured into a combined melts and solids (CMS) test fixture, and then allowed to cool to room temperature. Testing was done on a Rheometrics Dynamic Analyzer, RDA II. The CMS fixture consists of a cup 42 mm in diameter and a bilevel plate that has a serrated surface 8 mm in diameter concentric with and projecting from a plate 25 mm in diameter. Curves for  $G''/\sin\delta$  (i.e.  $1/J''$ ) were generated using values of  $G''$  and  $\delta$  measured from temperature sweeps between 52°C and 70°C at 10 rad/sec, taking a measurement every 6°C after a soak time of 2 min.

#### Fracture Toughness

The elastic fracture toughness,  $K_{Ic}$ , was determined according to procedures based on ASTM E399-90 (22). A notched asphalt beam was cast in a silicone mold, cooled, removed, and left for a minimum of 12 hr at -20°C before being tested under temperature-controlled conditions in an MTS Sintech 2/G test frame. The beams were loaded in a three point bend configuration at 0.01 mm/sec until failure occurred. The failure load was then used to calculate the linear elastic fracture toughness. For a more detailed description of the experimental procedure, the reader is referred to a previous paper by the Lee and Hesp (23).

#### Strain Rate Sensitivity

Sample preparation was the same as that used for determining the fracture toughness except that for these tests the temperature was raised to -10°C. Various crosshead speeds were used to break the asphalt beams. Results are expressed as failure energy, which was

TABLE 1 Aggregate Gradation Used for All Mix Tests

Sieve Size	Percent Retained		
	Limestone Coarse Aggregate	Limestone Screenings	Natural Sand
1	-	-	-
7/8	-	-	-
3/4	-	-	-
5/8	-	-	-
1/2	1.3	-	-
3/8	30.9	-	-
4	91.9	7.6	1.7
8	95.4	35.8	7.5
16	96.7	59.7	14.0
30	97.5	75.9	30.0
50	98.0	85.6	62.2
100	98.4	91.7	93.1
200	98.7	94.7	98.4

taken as the energy under the stress-strain curve at various crosshead speeds. Plotting these data on a semilogarithmic graph shows a sharp transition from brittle to ductile behavior. The strain rate at which this transition occurs gives an indication of the yield characteristics of the binder.

#### Asphalt Concrete Mix Preparation

The aggregate used in the asphalt concrete mixes consisted of three components, namely, 45 percent coarse limestone aggregate, 15 percent limestone screenings, and 40 percent natural sand. The gradation for the aggregate mix is given in Table 1. The aggregate was heated for a minimum of 12 hr at a temperature of 175°C. The asphalt was heated to 160°C just prior to mixing with the aggregate. All mixes contained 6 wt percent binder on the aggregate, which previously had been determined to be the optimum for this aggregate gradation. Compacting was done by using a Rainhart Series 142 Gyratory Compactor set for 250 gyrations at an angle of 1°. The compaction temperature was 160°C for all mixes.

#### Asphalt Concrete Testing

##### Tensile Failure Strains

Small rectangular blocks measuring approximately 30 mm × 35 mm × 60 mm were cut from the large briquettes and epoxied between 20-mm-thick steel plates. The glue was allowed to harden for a minimum of 24 hr after which the samples were cooled in a freezer at the desired test temperature for a minimum of 12 hr.

The mix samples were tested in tension using a crosshead speed of 0.0025 mm/sec with a computer interfaced linear variable displacement transducer (LVDT) accurate to  $\pm 5 \mu\text{m}$  mounted on each side of the test specimen to measure the extension. The actual strain rate within the specimens was found to be comparable to that of typical shrinkage rates in pavements exposed to rapidly dropping temperatures during autumn and winter months. Failure strain values reported were calculated from the measured displacements, each value being the average of five tests, the value for each test being the average of the two sides.

## RESULTS AND DISCUSSION

### Devulcanization

Crumb rubber samples were devulcanized to determine the effectiveness of various devulcanization chemicals.

The devulcanization residues were analyzed by gel permeation chromatography to determine the molecular weight of the devulcanized rubbers and to see whether there is any difference between the effect of different devulcanizing agents. The data showed that there is not a great deal of difference between different devulcanizing chemicals. This may be explained by the selectivity of the devulcanization reaction for cleaving sulfide bonds only, leaving the backbone of the styrene-butadiene rubber intact. However, the different devulcanization agents give rather different yields. Table 2 gives the devulcanization yields for the reagents used in this study. These results show that the two thiophenol reducing agents are clearly the most effective on an equal weight basis. The order of effectiveness may change though when these products are compared on an equal cost basis.

TABLE 2 Solvent Devulcanization Yields

Additive	Active Ingredient (@ 10 wt % on the GRT)	Devulcanization Yield, %
None	-	0.0
4-Chlorothiophenol	-	84.1
MOTS No.1 Accelerator	50% Thiuram Disulfides	70.2
Renacit 7	Pentachlorothiophenol	85.3
Plastone	Complex Mixture	39.2
Leegen 6130	Sulfonated Products	75.7

It is important to note that none of the commercial devulcanizing agents are fully effective under these reaction conditions. It is therefore appropriate that further research into finding a more effective and economical process for the devulcanization of waste rubber be continued.

## Binder Performance

### High Temperature Performance

The high temperature performance for a number of control and rubber modified binders was determined according to SHRP procedures. Figure 5 gives the inverse creep compliance for both crumb and devulcanized rubber modified binders together with data for 85-100 and 150-200 penetration grade control binders. The addition of the reductively devulcanized rubber provides only a modest improvement to the 150-200 binder because of the low molecular weight of the devulcanized rubber. A hazard involved in this process is the degree of solvent removal; a small amount of residual solvent will have a large effect on the binder properties at high and low temperatures. It should be noted that the 150-200 control and the solvent devulcanized and crumb rubber systems may be compared with each other but may not be compared directly to the oxidatively devulcanized system and the 85-100 control because of the differences in penetration grades. A stiffer binder will naturally perform better at high temperature, so at best one may only examine relative increases of modified binders of different penetration grades over their respective unmodified binders.

### Low Temperature Performance

The low temperature fracture resistance for crumb and devulcanized rubber modified binders was determined in a notched three point bend test. The average fracture toughness was calculated from the failure loads of approximately 10 to 20 samples.

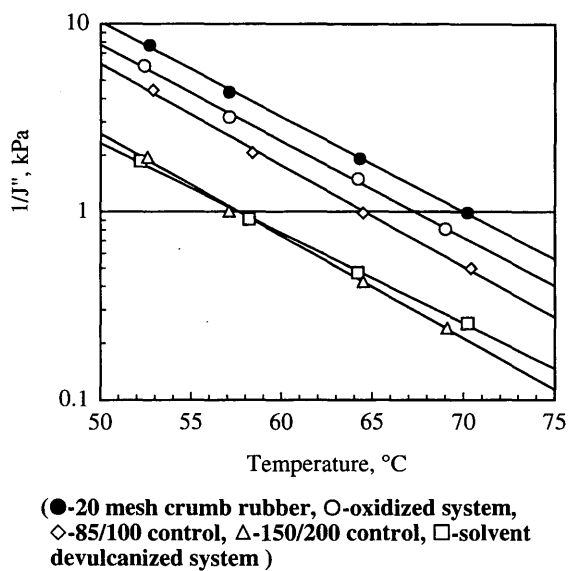


FIGURE 5 Inverse creep compliance for rubber modified asphalt binders.

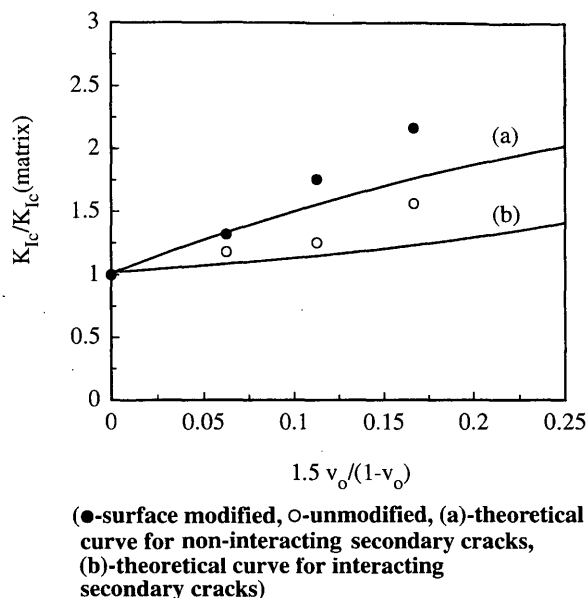


FIGURE 6 Relative fracture toughness increase in crumb rubber modified asphalt binders.

Figure 6 gives the relative improvement in fracture toughness of the crumb rubber modified binders over the matrix fracture toughness as a function of the volume fraction  $v_o$  of rubber in the matrix. This graph includes the theoretical contribution to the fracture toughness from crack pinning effects. The crumb rubber particles form obstacles for a propagating crack front and therefore pin the crack and produce a tougher binder. The fracture toughness increase in the presence of the obstacles is now determined by the load required to propagate a series of secondary cracks bowing out from between the particles. A more extensive discussion on the crack pinning theory appears elsewhere (24). Figure 6 does show, however, that the cause for the increase in fracture toughness in these systems is due to both crack pinning and viscoelastic effects. The energy consumed to produce the new fracture surfaces is dissipated through viscous and elastic flow mechanisms. The surface grafting of the polybutadiene onto the crumb rubber particles improves the fracture toughness substantially (Figures 1 and 6) owing to the additional viscous energy that is dissipated when the well-bound particles are pulled out from the fracture surfaces. For the unmodified crumb rubber systems, this effect is not present and particles can easily debond from the matrix allowing cracks to propagate at much lower stress levels.

In the case of devulcanized rubber binder systems the crack pinning mechanism is not occurring simply because there are no obstacles to pin the propagating crack front. Increases in fracture toughness for such systems can be attributed solely to enhanced shear yielding of the matrix and localized yielding in front of the propagating crack tip, whereas unmodified asphalt fails in a brittle fashion. Figure 7 gives the fracture toughness for the oxidatively devulcanized rubber and the fracture toughness for the solvent devulcanized systems. The fracture toughness for two control binders is also given for comparison. These data show that the relative increase in low temperature performance is much higher for the solvent devulcanized system than the oxidatively devulcanized system because of the adverse effect of the oxidative air-blowing process on the binder, a fact that is well known in the literature (25).

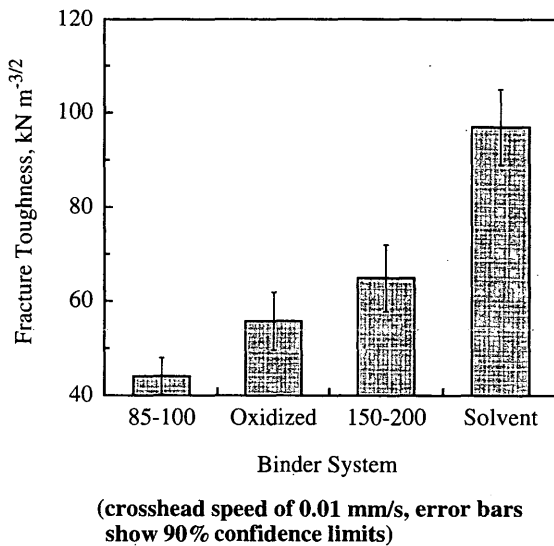


FIGURE 7 Fracture toughness for rubber modified binders at -20°C.

#### Variable Strain Rate Tests

The fracture toughness test was conducted at various strain rates at -10°C to learn more about the yield behavior of the rubber modified binders. At low temperatures the pavement shrinks and the asphalt binder may allow for yielding to release the thermal stresses. Binders that yield at higher rates of thermal shrinkage and at lower temperatures are more favorable for use in cold climates.

Figures 8 and 9 give the failure energy as a function of the strain rate for 85-100 and 150-200 grade control binders, unmodified crumb, surface modified crumb, solvent devulcanized and oxidatively devulcanized binders. From these results it is apparent that the position of the brittle-to-tough transition is shifted by the addition of rubber to the binder.

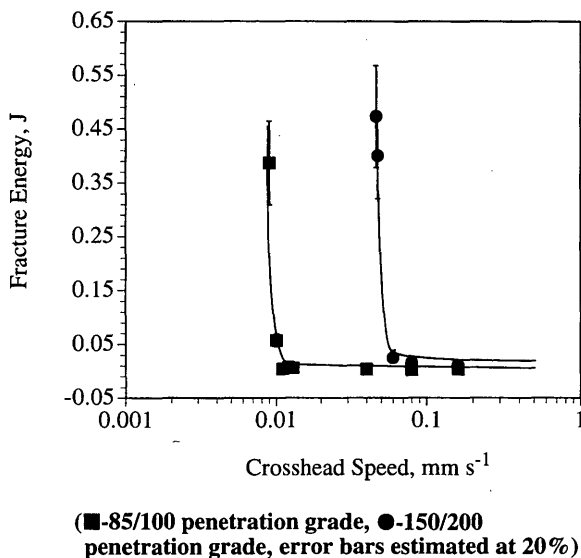


FIGURE 8 Brittle-to-ductile transition for bow river source asphalts.

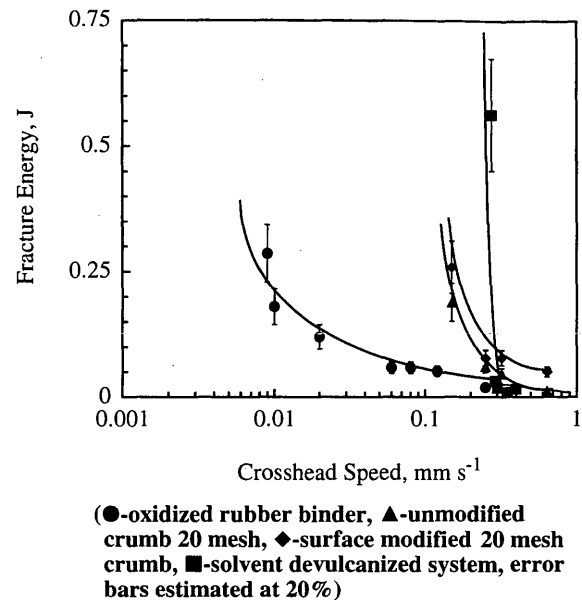


FIGURE 9 Brittle-to-ductile transitions for various rubber modified binders.

#### Asphalt Concrete Tests

Eventually it matters most how rubber modified binders perform in a pavement on a road subjected to both environmental and traffic-induced distress mechanisms. For this reason many paving authorities are using test sections to evaluate polymer and rubber additives. However, obtaining results from test sections can take several years; therefore, laboratory tests are often used to simulate extreme pavement conditions to obtain accelerated performance results. One of the main problems with laboratory tests is their inability to simulate true distress conditions.

In this work we have measured the failure strains for a number of crumb and devulcanized rubber modified binders in order to compare the different binders. Figure 10 shows the results for crumb rubber and surface-grafted crumb rubber, solvent-devulcanized and oxidatively devulcanized binders, respectively. The solvent-devulcanized system shows the highest failure strain, which can be explained by this binder's lower modulus and higher fracture toughness. The data also show that there is no great difference between the surface-modified and the unmodified crumb systems. This may be due to the type of failure in the mix; further research should look at this in more detail. Finally, the oxidatively devulcanized binder shows the lowest failure strains at all temperatures.

#### CONCLUSIONS

The properties of several rubber modified asphalts have been evaluated at high and low temperatures. High temperature inverse creep compliance values of the modified binders show modest improvement for a solvent devulcanized rubber and good improvements for crumb and oxidatively devulcanized rubbers. Relative increases in low temperature fracture toughness of the modified over unmodified binders show large differences, with the solvent-devulcanized rubber imparting a greater improvement. Data on the low temperature failure strains of mix specimens prepared from the modified

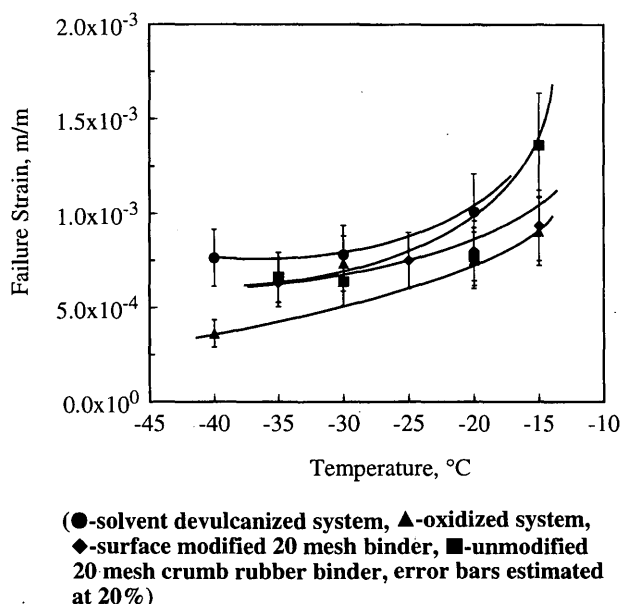


FIGURE 10 Failure strains for rubber modified asphalt concrete samples.

binders are presented, revealing the greater susceptibility of the stiff, oxidatively devulcanized rubber system to thermal stress induced cracking. The two crumb rubber systems perform very similarly, while the mix made with the reductively devulcanized rubber modified binder shows the highest failure strains.

#### FURTHER WORK

The results of this research indicate that the devulcanized rubber modified binders have the potential to give improved low temperature performance. An economical and environmentally acceptable process should be developed to produce such binders. These systems would have the advantage of being stable during storage at high temperatures.

Further work should continue by investigating mix performance. Thermal stress restrained specimen tests that reflect thermal shrinkage, stress relaxation, and failure characteristics may give an indication of how these rubber modified binder systems change the brittleness temperature of the mix.

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#### REFERENCES

1. Pub. L 102-240, 18 December 1991, *Intermodal Surface Transportation Efficiency Act of 1991* (ISTEA). 105 Stat. 1914.
2. Roberts, F. L. *Investigation and Evaluation of Ground Tire Rubber in Hot Mix Asphalt*. National Center for Asphalt Technology, Auburn University, Alabama, 1989.
3. Esch, D. C. *Asphalt Pavements Modified with Coarse Rubber Particles—Design, Construction and Ice Control Observations*. Report FHWA-AK-RD-85-07. FHWA, U.S. Department of Transportation, 1982.
4. Heitzman, M. An Overview of the Design and Construction of Asphalt Paving Materials with Crumb Rubber Additive. Presented at 71st Annual Meeting of the Transportation Research Board, Washington D.C., 1992.
5. Rouse, M. W. Improved Rubber Asphalt Mix. World Patent Application, PCT Int. Appl. WO 9314156 A1, 22 July 1993.
6. Joseph, P. E. and G. Kennepohl. *Trial Section with Polymer-Modified Asphalts on Highway 400*. Report PAV-91-03. Ministry of Transportation of Ontario, Downsview, Ontario, Canada, June 1991.
7. Page, G. C., B. E. Ruth, and R. C. West. *Florida's Approach Using Ground Tire Rubber in Asphalt Concrete Mixtures*. Transportation Research Board 71st Annual Meeting, January 12-16, Washington D.C., 1992.
8. Hui, J., G. R. Morrison, and S. A. M. Hesp. Improved Low Temperature Fracture Performance for Rubber-Modified Asphalt Binders. In *Transportation Research Record 1436*, National Research Council, Washington D.C., 1994, pp. 83-87.
9. Scott, C. E. Waste Rubber Disposal. U.S. Patent, US 3700615, 24 Oct. 1972.
10. Winters, R. E., and C. H. McDonald. Pavement Composition. U.S. Patent, US 3919148, 11 Nov. 1975.
11. Nielsen, D. L., and J. R. Bagley. Rubberized Asphalt Paving Composition and Use Thereof. U.S. Patent, US 4068023, 10 Jan. 1978.
12. Davis, F. R. Modifying Asphalt with Thermoplastic Polymers, Ground Rubber and Compositions Produced. U.S. Patent, US 4485201, 27 Nov. 1984.
13. Causyn, D. W., and K. Thys. Recycled Rubber in a Polymer Modified Asphalt and a Method of Making Same. World Patent, PCT Int. Appl. WO 92/21820, Dec. 10, 1992.
14. Liang, Z. Z., and R. T. Woodhams. Treatment of Rubber to Form Bituminous Compositions. World Patent Application, PCT Int. Appl. WO 94/14896, July 7, 1994.
15. Porter, M. Vulcanization of Rubber. *Organic Chemistry of Sulfur* (S. Oae ed.), Plenum Press, New York, N.Y., 1977, p. 75.
16. Oae, S. *Organic Sulfur Chemistry: Structure and Mechanism*. CRC Press, Boca Raton, Fla., 1991.
17. Schmidt, W., J. Miketta, and E. Kamper. Storable Bituminous Binder for Paving Purposes. German Patent, DE 1594756, 13 Dec. 1973.
18. Biegenzein, G. Method and Apparatus for Preparing a Bituminous Binder. U.S. Patent, US 4314921 A, 9 Feb. 1982.
19. Hoehr, D., K. Bergmann, H. Vonk, and A. Taube. Storable Polymer-Modified Bitumen. German Patent, Ger. Offen. 3819931 A1, 14 Dec. 1989.
20. Duong, Q. D., and R. Boisvert. Manufacture of Homogeneous Asphalt Compositions, and the Compositions Obtained. World Patent, PCT Int. Appl. WO 9317076 A2, 2 Sept. 1993.
21. Jung, D., and T. Vinson. Low Temperature Cracking Resistance of Asphalt Concrete Mixtures. *Journal of the Association of Asphalt Paving Technologists*, Vol. 62, 1993, pp. 54-92.
22. Standard Test Method for Plain-Strain Fracture Toughness for Metallic Materials, ASTM E 399-90, In *1992 Annual Book of ASTM Standards*,

- Part 10, American Society for Testing and Materials, Philadelphia, 1992, pp. 506–515.
23. Lee, N. K., and S. A. M. Hesp. Low Temperature Fracture Toughness of Polyethylene-Modified Asphalt Binders. In *Transportation Research Record 1436*, TRB, National Research Council, Washington, D.C., 1994, pp. 54–59.
24. Rodriguez, M. G. *Crack Pinning in Particulate Filled Asphalt Binders and Hot Mix Asphalt Concrete*. MS thesis Queen's University, Kingston, Ontario, Canada, 1995.
25. Jung, D., and T. Vinson. Low Temperature Cracking Resistance of Asphalt Concrete Mixtures. *Journal of the Association of Asphalt Paving Technologists*, Vol. 62, 1993, pp. 54–92.

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