EFFECTS OF RUBBER ADDITIVES ON PROPERTIES OF ASPHALTIC MATERIALS

BY

JOHN ALBERT ALEXANDER B.S.C.E., Purdue University (1956)

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering

at the

Massachusetts Institute of Technology

(August 1968)

A. A AA

Signature of Author . . Department of Civil Engineering, August 17, 1968

Certified by . . .

Thesis Supervisor

ABSTRACT

EFFECTS OF RUBBER ADDITIVES ON

PROPERTIES OF ASPHALTIC MATERIALS

Ъy

JOHN ALBERT ALEXANDER

Submitted to the Department of Civil Engineering on August 17, 1968, in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering.

This study investigated the modification of asphalt with various rubbers and the effect of this modification on the values of fracture toughness at low temperature.

Test results indicated that the fracture toughness of asphalt can be substantially increased by modification with a small percent of either a suitable rubber in latex form or with a low molecular weight liquid rubber that is crosslinked after dispersion by the use of an epoxy and hardener.

The effects of an accelerated aging procedure on the modified asphalts revealed that the prolonged exposure to high temperature further increased the fracture toughness while fracture toughness of unmodified asphalt was lowered by exposure to the same aging procedure.

Addition of mineral filler increased the flexural strength of the test beams but did not significantly change the fracture toughness of the modified asphalt.

A brief study of the various modifications at the magnifications provided by the optical microscope revealed a strong relationship between the fineness of the rubbery second phase and the values of critical strain energy release rate.

Thesis Supervisor: Title:

Fred Moavenzadeh, Ph.D. Associate Professor of Civil Engineering

ACKNOWLEDGEMENTS

The author is very grateful to Professor Fred Moavenzadeh, thesis supervisor, for his guidance and encouragement during this research project.

The author would also like to thank the manufacturers mentioned in the text for technical advice and the material samples used in the study.

TABLE OF CONTENTS

																								Page
Title	Page	•	•	•	•	•	•	•	•	•	•	•	è	•	•	•	•	٠	•	•	•	•	•	1
Abstra	ct.	•	•	•	•	•	•	•	•		•	•	•	•	•		÷	•	•	•				2
Acknow	ledge	me	nt	S	•	•		•	•	•	•		•	•			•			•	•			3
Body c	f Tex	t	•	•	•	•	•	•	•	•		•	•	•										24
I.	Intr	٥d	uc	ti	or	1	•			•		•	•	•		•				•	•	•		4
II.	Prev	rie	W	of	' I	jit	ter	rat	tui	re			•				•		•		•	•		7
	Pr	rev Pa					.b.	ies	5 (of	Cr	rac	k	Lng	g (of	As	pł	n a]	t	•	•	•	7
	Br	it	tl	е	Fr	a	eti	are	Э						•		•	•	•					8
	Br	it	tl	е	Fr	a	eti	are	е :	in	Pc)]3	rme	eri	Lc	Ma	ate	r	La]	s	•			12
	Ru	ibb	er	Μ	lođ	11	(ie	ed	As	spł	n a 1	Lts	3	•			•		•					15
III.	Obje	ect	iv	е	ar	nd	S	or	pe	•	•		•	• -		•	•				•	•		17
VI.	Mate	ri	al	ន			•	•	•	•	•			•			•				•		•	19
	As	sph	al	t	•		•	•		•	•	•		•							•			19
	Ru	ibb	er		•	•		•	•		•		•	•	•	•		•	•		•			20
	Ag	gr	eg	at	e	•			•		•			•						•				21
v.	Proc	eđ	ur	е	•			•	•		•	•	•	•	•	•	•			•				23
	Nc	otc De									eci	me	en	ar	nd	Te	•xt	•	•	•	•	•	•	23 23
		Mi	xi	ng	a	nc	3	Spe	ect	Lme	en	Pr	rer	bar	ra t	cic	n			•				24
		Ag	in	ġ	•	•	•		•	•	•			•				•				•		25
		Те	st	in	g					•	•			•					•			•		26
		Co	mp	ut	at	ic	n	of	C (3	•	•	•						•					26
	Shee									C		•	•	•					•				•	27
		M1	x	Pr	ep	aı	rat	tic	on			•												27
		Sp	ec	im	er	ı I	Pre	epa	ara	ati	Lor	J		•				•	•					28
		Te	st	in	g	•	•					•		•							•	•		2 9
	Micr	'08	co	pì	с	St	cu	Ĵу			•		•		•		•	•	•		•		•	29

Page

VI. F	lesults	and l	Disc	uss	510	n	•	٠	•	•	•	•	•	•	•	٠	•	-	•	31
	Prelim	inar	y Re	sul	lts		•	•	•	•			•		•	•	•	•	•	31
	Effect	of	L-17	0	•	•	•	•	•	•	•	•	•	•	•	•	•		•	33
	Effect	of	CTBN		•	•	•	•	•	•	•	•			•	•	•		•	34
	Effect	of	Temp	era	itu	re		•	•	•	•		•	•		•	•	•	•	34
	Effect	of	Mine	ra]	l F	11	le	r	•	•	•	•	•		•	•	•	•	•	35
	Effect	of.	Agin	g	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	37
	Sheet	Asph	alt	•	•		•	•	•	• .	•	•	•	•	•		•	•	•	40
	Micros	copi	с.	•	•		•	•	•	•	•	•					•	•		41
	Cost C	ompa	risc	ns	•	•	•		•	•	•		•		•	•			•	43
VII. C	Conclusi	ons		•		•	•	•	•	•	•	•		•		•	•	•	•	46
Reference	s	• • •		•	•	•	•	•	•	•	•	•	•	•	•	•	•		•	48
Tables (8	3)			•	•		•	•	•	•		•	•	•		•			•	53
Figures (10)	• •		•	•		•	•	•	•	•	•	•	•	•	•		•	•	59
Appendice	s	• •	• •	•	•	•	•	•	•	•	•	•	•	•	•	•	•		•	68
A. Def	inition	of	Symb	ols	3	•	•	•			•	•	•	•					•	69
B. Lis	st of Ta	bles	•••		•	•	•	•	•		•	•	•		•	•	•		•	70
C. Lis	t of Fi	gure	s.									•		•						71

I. INTRODUCTION

Cracking of asphaltic pavements is one of the most common defects leading to unserviceability and a premature need for resurfacing. For this reason, resistance to cracking is an important characteristic of asphaltic paving mixtures. Cracking itself is not too important, since a cracked pavement may ride as well as an uncracked one. What is important is the secondary distress that results from cracking.

Cracks provide access points to the base and subbase for water which can cause softening and loss of strength. Cracks also reduce the load distributing capability of the wearing surface which leads to greater stress concentrations in the base layers. These stress concentrations in turn increase the deformations which cause more cracks to develop. After the cracks become closely spaced, the opportunity for raveling and spalling is increased, leading to eventual failure of the pavement.

Although the importance of cracking has long been recognized there is, at present, no quantitative measure of crack resistance or fracture toughness available for specifying asphalt or for use in the design of paving mixtures. A quantitative measure is also needed to evaluate the effectiveness of changes in the asphalt or asphaltic mixture. These changes might be studied as a means of improving the crack susceptability of asphalt.

In recent, experimental, attempts to provide this type of quantative measure, the critical strain energy release rate (G_c) has been used as a measure of asphalt's crack resistance (1)*.

-4-

*Numbers in parentheses refer to references.

The cracking of asphalt pavements can be considered as two interrelated problems. First, the inherent crack resistance of the compacted paving mixture at the time of construction. Second, the aging and embrittlement of the asphaltic mixture during service which leads to cracking and a shortened useful life even for pavements that originally had satisfactory crack resistance. Any effective attempt to improve the crack resistance of asphaltic mixtures must consider both of these problems.

Several of the studies referred to in the review of literature indicate that modification of asphalt using a rubber additive may improve the fracture toughness of asphalt and asphalt mixes as well as reducing the embrittlement due to aging (2,3,4,5,6).

In this study, the effects of rubber modification on fracture toughness and resistance to aging of asphalt are investigated. A technique developed to find the critical strain energy release rate is used to measure the fracture toughness.

Many factors influence the crack resistance of asphaltic concrete. Gradation and quality of aggregate, properties of asphalt, permeability of mixture, mixing temperature, climate, and thickness of the layer all have their effect.

However, since the mechanical strength of the aggregate is greater than the cohesive forces of the asphalt, the asphaltic mixture usually cracks either through the asphalt phase or at the boundary between aggregate and asphalt (7,8). The asphalt thus plays a major role in the crack resistance of the asphaltic mixture, and it seems logical that some measurable property of the asphalt should correlate with the crack resistance of the asphalt-aggregate mixture.

-5-

Another reason for measuring a property of the asphalt itself instead of a property of the completed mix is the elimination of the variables introduced by the design and construction of the mix. If these are not held constant from test to test, their influence on the potential crack resistance of the asphalt mixture may obscure the influence of the asphalt itself.

For the above reasons, most of the tests made during this study to evaluate the effects of rubber modification were performed on specimens of asphaltic cements instead of on asphalt-aggregate mixtures.

-6-

II. REVIEW OF LITERATURE

This review of literature is divided into four sections. Each section includes a review and discussion of literature that was found pertinent to the study. These sections include review of;

- A. previous studies of cracking of asphalt pavements.
- B. the concept of fracture mechanics and the use of strain energy release rate as a measure of fracture toughness of asphalts.
- C. fracture behavior of other polymeric materials.
- D. work on rubber modification of asphalt.

Relationship Between Asphalt Properties and Cracking of Pavement.

Since cracking has long been recognized as a problem of asphalt pavements there have been attempts to correlate conventional asphalt tests with resistance to cracking.

These studies have produced a considerable amount of data on the cracking of asphaltic mixtures but have not resulted in a correlation between asphalt properties and resistance to cracking that can be used by the highway engineer for specifying asphalts or designing asphaltic mixtures.

Penetration is a common test that has been suggested as a method of predicting resistance to fracture. Comparisons of original penetration values with cracking of observed test sections have indicated that penetration by itself is an unreliable indicator of cracking resistance, (9). However, there does seem to be a relationship between the cracking of asphaltic pavements and the penetration of asphalt recovered from the cracked pavements (10).

Ductility has also been noted to be somewhat related to fracture resistance, (9). However, no reliable relation-

-7-

ship has been determined.

Viscosity has also been used in attempts to predict crack susceptibility. Some correlation between viscosity and cracking was found but the relationships were complicated by the temperature sensitivity factor (11). Although two asphalts might have the same viscosity at normal temperatures, the one with the higher temperature sensitivity will possibly become more brittle at low temperatures.

Because of this temperature sensitivity problem there is some evidence that the glass transition temperature may be a more accurate indicator of cracking resistance than viscosity, (12).

In addition to the attempts to predict fracture resistance by the use of standard tests, special tests have been devised specifically for this purpose.

These have included tests using special apparatus to find values of test results under various conditions (9,13). As with the study of standard tests, results of these studies have also been inconclusive.

All of these studies have provided useful information about the fracture behavior of asphalt and asphaltic mixes, none of them, however, has resulted in the measurement of an inherent property of the material that could be used to predict the resistance to cracking of the completed asphalt pavement.

Brittle Fracture

Asphalts behave as brittle glassy solids at the low temperatures where they are most susceptible to cracking. This suggests the possibility that the theory of brittle fracture may be used to measure their crack resistance.

-8-

The theory of brittle fracture was developed to explain the observed difference between the theoretically calculated strength and the experimental strength of brittle materials. The theoretical strengths, computed from the forces needed to separate the atomic bonds, are usually 10 to 100 times greater than the values determined experimentally.

This difference between the observed and theoretical strengths is considered to be due to nonuniform distribution of stresses in the materials. Flaws of various kinds are inherent in all materials. These flaws cause stress concentrations much higher than the measured stress for the entire sample. As these concentrated stresses reach the true tensile strength for the material, a crack starts, and as the sharp tip of the crack advances, a continuing point of high stress concentration is provided. In this way a brittle material can fracture at an observed stress far below the theoretical strength of the material.

An elastic body which is deformed by an applied load has stored energy as a result of the induced strain. If a crack results from the applied load, some of this energy is released. This can easily be visualized by considering that if the elastic body fractures completely, there will be no more energy stored as a result of the load.

Griffith (14,15) explained the fracture behavior of a brittle material by considering an infinite plate of unit thickness with a sharp crack 2c long. He determined that the excess strain energy of this plate without a crack over the energy of the same plate with a sharp crack of 2c length was:

$$\Delta U = \frac{\pi c^2 \sigma^2}{E}$$

-9-

Eq. 1

Where σ is the stress in the plate and E is the modulus of elasticity.

If the crack is extending on both ends, four new surfaces are being created. The work required to create these surfaces is:

$$\Delta T = 4\gamma c$$

Eq. 2

Where γ is the surface energy of the material per unit area.

If the amount of strain energy releated by the advancing crack (ΔU) equals the amount of work required to form new surfaces (ΔT) for a small increase in crack length, then the crack will extend rapidly and cause failure. This can be represented by

$$\frac{\mathrm{d} W}{\mathrm{d} \mathrm{c}} = \frac{\mathrm{d} (\Delta \mathrm{T} - \Delta \mathrm{U})}{\mathrm{d} \mathrm{c}} = 0$$

by substitution

 $\frac{\pi c\sigma}{E} = 2\gamma$

Solving for the stress required to reach this critical failure condition gives the Griffith formula:

$$\sigma = -\sqrt{\frac{2\gamma E}{\pi c}}$$

Eq. 3

For plane strain (thick plate) E must be replaced with $E/(1-\hat{F})$, where μ is Poisson's ratio. This gives the

-10-

following expression for the critical stress

$$= \sqrt{\frac{2\gamma E}{\pi (1-\mu^2)c}}$$

Eq. 4

Eq. 5

Irwin (16) suggested a form for expressing the true driving force for crack propagation in a brittle material. He noted that equating the strain energy derivative to the surface energy derivative results in the critical stress for failure only if all contributions to energy dissipation are included as surface energy. Irwin simply took the derivative for Equation 1 which gives the strain energy release rate:

$$G = \frac{dU}{dc} = \frac{2\pi c\sigma^2}{E}$$

The value of the strain energy release rate at the start of unstable crack propagation is called the critical strain energy release rate, G_c . Irwin (17) suggested that the critical strain energy release rate should be a constant for the material, since different loadings can produce the same stress concentration at the tip of the crack.

It has been found that at low temperatures, the Griffith Theory of brittle fracture can be used to study the fracture behavior of asphalts and that the critical strain energy release rate is independent of the geometry of the specimen, (1).

Notched beams tested in bending can be used to determine the critical strain energy release rate for asphalt (1, 18).

-11-

The right side of equation 5 must be divided by two since a notched instead of an interior crack is used and only two surfaces are formed. The dimensions of the beam also make it necessary to substitute $E/(1-\mu^2)$ for E since a state of plane strain exists. The resulting expression for the strain energy release rate is:

$$G = \frac{\pi(1-\mu^2)c\sigma^2}{E} \qquad Eq. 6$$

This equation is used as modified by Winnie and Wundt (19) for rectangular beams:

$$G = \frac{(1-\mu^2)\sigma_n^2 h}{E} f(c/d)$$
 Eq. 7

Where σ_n is the nominal bending stress at the root of the notch, f(c/d) is a function of the notch depth to beam depth ratio and h is the net depth of the beam at the notch. When the nominal bending stress at the root of the notch is that necessary to cause rapid crack, propagation to failure, equation 7 gives values of the critical strain-energy release rate (G_c). This is the expression used during this study as a measure of the resistance of asphalt to brittle failure.

Brittle Fracture in Polymeric Materials

Asphalt is an amorphous polymeric material, composed of randomly oriented long chain molecules, similar to many common synthetic polymers, such as polystryene, polymethyl methacrylate polyester and epoxy.

The fracture of synthetic amorphous polymers has been studied extensively during the last five years. A brief discussion of some of this work will be included since the

-12-

behavior of asphalt is similar to the behavior of these synthetic polymers or plastics.

Amorphus polymers generally behave as elastic isotropic solids at temperatures below their glass transition temperatures, and usually fracture in a brittle manner at these low temperatures. The theory of brittle fracture has been successfully applied to the study of fracture of synthetic polymers, (20,21).

Above the glass transition temperature amorphous polymers display viscoelastic characteristics, and they may fail in a brittle manner at sufficiently high strain rates.

A number of criteria are available to determine whether a material has failed in a brittle manner. These included criteria based both on changes in the shape of the sample during failure and on the shape of the force deflection relationship.

Brittle failure is characterized by uniform deformation of the specimen up to the point of fracture where rapid crack propagation causes failure of the specimen. The fractured sample should show no observable, residual, strain indicating significant macroscopic plastic flow and the force deflection curve should be linear to the point of failure (20).

These criteria were used in this study to judge the applicability of brittle fracture theory to the asphalts tested.

Recent studies on plastics have shown that although many of them exhibit brittle fracture, most of the work required to cause fracture is absorbed by the microscopic cold drawing and plastic flow of the material which takes place near the advancing crack tip (21). This results in a thin

-13-

layer of material on the newly formed surfaces which has been oriented by the stress field near the advancing crack tip. Since the measured surface energies of the plastics studied were 1000 times the theoretical surface energies computed by considering the force needed to break the molecular bonds, (21); it is believed that the molecular reorientation consumes a major part of the work required to fracture.

Another factor that makes the review of fracture of synthetic polymers of particular interest to this study is the method used to modify some of them for increased fracture toughness. This modification consists of suspending a low concentration of rubber in the plastic as small discrete particles. This modification is used commercially for toughening thermoplastics such as polystyrene and polymethyl methacrylate, and more recently has been found to be capable of toughening thermosetting plastics such as polyester and epoxy (22,23).

The mechanism responsible for this toughening by a rubbery second phase has been explained to be due to the crack inhibiting properties of the rubber inclusions (24). It was thought that as the crack traveled through the brittle plastic matrix the rubber particles encountered tended to prevent the crack from opening and thus increased energy was required to fracture the modified material.

However, more recent studies on both thermoplastics and thermosetting plastics have indicated that another mechanism is responsible for the toughening (23,24). Study of stressed, rubber modified, plastics with both phase-contrast and polarized light microscopy reveals that bands of oriented polymer are present at right angles to the direction of stress. These bands represent a significant volume of the

-14-

stressed area and not limited to the immediate area of the crack.

As a result of these observations, the toughening of brittle plastics with rubber plastics is now explained on the basis of the energy required to orient relatively large volumes of the matrix material.

Since the rubber, or rubber-plastic, particles have a much lower modulus of elasticity than the matrix, stress causes the development of a non-uniform stress field. The plastic matrix is oriented progressively in the areas of higher stress concentration and these areas can then be observed as stress whitened or crazed areas. The orienting or crazing involves plastic flow and since a successfully toughened plastic will have an appreciable volume of material oriented by stress, a relatively large amount of energy is absorbed. This high energy absorption accounts for the high fracture toughness of these materials (25).

Rubber Modified Asphalts:

The crack resistance of an asphalt pavement depends on many factors involving mix design and construction practice but the characteristics of the asphalt cement itself play a major role since the cracking actually takes place through this phase of the paving mixture (7,8,9). For this reason, improvement of the properties of asphalt offers the possibility of major improvement in the resistance to cracking of paving mixtures.

Modification with rubber has been used to change the various properties of paving asphalt. A variety of different procedures have been used to modify asphalt with rubber. Natural, reclained, and several types of synthetic rubber have been added to asphalt in many forms including; powders, solutions, latexes, and premixed masterbatches of rubbers and asphalt (3,4,26,31).

These modified asphalts were tested in various ways for changes in properties. Standard ASTM tests for penetration, softening point and ductility were used as well as some special tests which were devised especially to measure the changes in properties caused by the rubber modification (2,4).

Tests on rubber modified asphalts usually indicated that the modification reduced penetration and flow and increased ductility, softening point, toughness, tenacity and torsional recovery (3,4).

Tests on compacted mixtures of aggregate and modified asphalt have indicated that the resistance to failure by repeated flexing, as might be experienced under traffic, is significantly increased by the rubber modification, and that this increase is reduced, but still significant, after aging (6).

Paving mixtures modified with rubber are apparently practical to construct without highly specialized equipment since most of the reports reviewed indicated that there is little difficulty in constructing this type of surface (27,28,29).

Difficulties that have occasionally occurred and should be avoided include:

- A. pulling under the screeds of the paving machine if an excess of rubber is used (28).
- B. depolymerization of rubber at temperatures over $375^{\circ}F$ (28).
- C. compaction difficulty for mixtures modified with powdered asphalt (30).

Other than these limitations, construction of rubber modified asphalt appears to present few construction problems.

III. OBJECTIVE AND SCOPE

The objective of this study was to investigate the effect of a rubbery second phase on the low temperature fracture toughness of asphaltic cement.

Particular emphasis was placed on determining if this change in fracture toughness was still effective after the asphalt was exposed to an accelerated aging procedure.

A secondary objective was to investigate the possibility of introducing a rubbery second phase in asphalt by polymerizing and cross-linking a liquid rubber that had been finely dispersed in the asphalt. This was tried as a means of producing a second phase that would improve the fracture toughness more than could be achieved by adding the rubber in latex form.

In order to meet the above objectives, a laboratory investigation was made as outlined below.

The major part of the study involved bending tests on small beams of asphalt at low temperature to determine the values of G_c as a measure of fracture toughness.

A series of preliminary tests were made to select combinations of asphalt and rubber for further study. Two asphalts and five rubbers were studied and one asphalt and two rubbers were selected for additional testing. The selected asphalt, modified with each of the two rubbers was then tested at different temperatures and concentrations. These tests included both unaged and aged asphalts as well as specimens made with and without mineral filler.

In addition to the tests used to measure the fracture toughness parameter, a limited number of tests were also run on cylinders of compacted sheet asphalt made with the rubber

-17-

modified asphalt. These were made to determine the changes in compressive strength and maximum deflection that could be expected as a result of rubber modification.

A study of the microscopic variations in the modified asphalts was also made to aid in understanding the way in which rubber modification affects asphalt properties.

IV. MATERIALS

A. Asphalt

The two AC-20 grade asphalt cements used in this study were both used in the "Asphalt Institute-Bureau of Public Roads Cooperation Study of Viscosity-Graded Asphalts". The two asphalts were coded B-2960* and B-3056** by the Bureau of Public Roads. Properties of these asphalts are given in Table 1.

The dim	ASPHALT					
TEST	B - 3056	B-2960				
Specific Gravity	1.020	1.03				
Softening Point, Ring and Ball		125 ⁰ F				
Ductility 77°F	250+cm					
Penetration 200gm, 60 sec., 39.4 ⁰ F	30					
Flash Point, Cleveland Open Cup	545 ° F	515 ⁰ F				
Glass Transition Temperature***	-1.3 ⁰ F	-20.2 ⁰ F				
Viscosity at 140°F, poises x 10^2 ***	26.8	20.6				

Table 1: Results of Typical Tests on Asphalts Used in this Study.

*Produced by the Shell Oil Co. **Produced by the American Oil Co. ***Reference 32.

B. Rubber

Four of the five rubbers used for this study were in the form of latexes when introduced into the asphalt. Latex is the form of the raw rubber as it comes from the tree and consists of a suspension of colloidal sized rubber particles in water. Various types of synthetic rubbers are also made in latex form.

This is a convenient physical state for combining rubber into asphalt since both the small particle size and the liquid form aid the dispersion process. Latex is typically 30% to 40% rubber and 70% to 60% water. As the latex is introduced into the hot asphalt, this water is removed by boiling. The steam escaping from the asphalt causes foaming. In some instances, this foaming may limit the rate at which the latex may be mixed into the asphalt.

The L-170 and the natural rubber latexes used in this study were prepared with 72% and 62% respectively of rubber solids which reduced the problem of water removal.

Four rubber latexes were used during this study. Two were terpolymers of butadiene, styrene and vinyl pyridine with properties as follows:

- 1. (2508)* Fatty acid type emulsified pH 9.0
 Mooney Viscosity (ML-4 at 212^oF) = 90-120
 Percent solids 32%
- 2. (2518)* Rosin acid type emulsified pH 10.0
 Mooney Viscosity (ML-4 at 212^oF)= 28-43
 Percent solids 41%

* Manufactured by the B.F. Goodrich Chemical Co.

The third latex and the one used for the major part of the experimental work was L-170,* an anionic copolymer of 70% butadiene and 30% styrene with 72% solids, a pH of 10, and a Mooney Viscosity (ML-4 at $212^{\circ}F$) of 100.

The fourth latex was a natural rubber,** which had been stabilized with 0.7% ammonia and had a pH of 10.4.

CTEN*** was the only rubber used that was not in latex form. **CTEN** is a random copolymer of 20% acrylonitrile and 80% butadiene, and is in liquid form, with a molecular weight of 3300. The type used in this study had carboxyl groups at each end of the chain molecules. The carboxyl groups act as reactive sites for cross-linking which can be initiated by the addition of an epoxy resin and an appropriate curing agent.

The epoxy resin used was Epon 828****, an epichlorohydrin/ bisphenol A product with an epoxide equivalent of 185-205. This is a representative polymer of its type.

The curing agent or hardener used was DMP-30****, a 2, 4, 6, tri (dimethylaminomethyl) phenol.

C. Aggregates

The aggregate used in the sheet asphalt met the specifications for sheet asphalt aggregate given by ASTM Specification D-1663-59T. Gradation used is given in Table 2. The mineral filler used was a flint powder with all particles passing the 200 mesh sieve.

*Manufactured by the Goodyear Tire and Rubber Co. **Lotol, L-6032, U.S. Rubber Co., Chemical Division *** Hycar CTBN, B.F.Goodrich Chemical Co. ****Manufactured by Shell Chemical Co., New York, New York

-21-

Sieve Size	ASTM Specification	Selected Gradation					
	D1663-59T	% Passing					
16	85-100	100					
30	70 - 95	75					
50	45 - 75	45					
100	20-40	26					
200	9-20	15					

Table 2. Gradation of Aggregate used in Sheet Asphalt

V: PROCEDURE

Preliminary tests were made on combinations of the previously mentioned materials to select the most promising for further study. As a result of these preliminary tests it was decided to limit the study to beams made of B-2960 modified with either L-170 or CTBN and epoxy.

This section describes the procedure used during the study for specimen preparation, testing and computation.

Notched Beam Tests

This test was used for both the preliminary testing and the complete series of tests on B-2960 modified with each of the rubbers used. Details of the test are as follows:

Description of Specimen and Loading Geometry: In order to find G_c for the various asphalt-rubber mixtures, 1/2 "X 1/2 "X 5" beams of the mixture were cast and tested at low temperatures in a midspan bending test as shown in Figure 1.

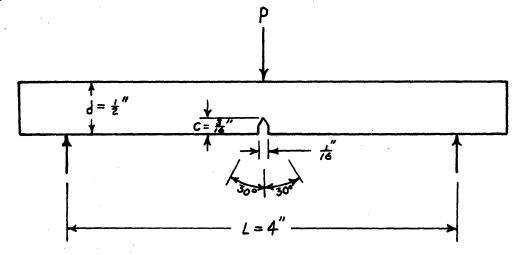


Figure 1: Beam Geometry and Method of Loading

Unnotched beams were used to find the modulus of elasticity, E, and a notch was cast in the beams used to find the tensile stress, $\frac{\sigma}{n}$. Once E and σ_n were determined, G_c was found by substituting the values of E and σ_n into equation 7.

Mixing and Specimen Preparation: Each test series included specimens modified with both 3% and 4.5% rubber. The percentages of rubber were based on weight of the asphalt and indicate solid rubber added not total weight of latex. When asphalt was modified with CTBN, epoxy was added in the proportion of one part epoxy for each three parts CTBN. Hardener was also added in the proportion of one part hardener for each 9 parts CTEN.

For modification with a rubber in latex form, the asphalt was heated in a thermostatically controlled oven at 140°C for one hour. The asphalt was then put in a mechanical mixer and mixed for three minutes. The rubber latex was poured into the asphalt; in a thin stream, during mixing. This facilitated the mixing action and also allowed the steam from the water in the latex to escape with a minimum of foaming of the asphalt. After the three minute mixing period, the asphalt was replaced in the oven (140°C) and heated for 20 minutes. The mixture was then mixed for another three minutes. After reheating in the oven for an additional 30 minutes, the beams were cast in metal molds. A coating of high vacuum grease prevented the asphalt from sticking to the molds. The molds were preheated in an oven at 140°C for 20 minutes immediately before casting.

The molds were filled above the top to allow for thermal shrinkage. After cooling to room temperature, the molds, now containing the asphalt were placed in a refrigerator and cooled to 5° C. The excess asphalt was then removed with a warm spatula, the molds were disassembled and the beams removed.

-24-

The beams were stored in covered containers at -10°C until tested.

For the asphalt modified with CTBN and epoxy, the procedure was slightly different. After heating the asphalt for one hour in the oven at 140°C, the CTBN and epoxy were added during a three minute mixing period. The asphalt was then reheated for 20 minutes. Another three minute mixing period followed during which the hardener (DMP-30) was added. The material was then reheated for 30 minutes and cast.

For the beams cast of asphalt and mineral filler, the mineral filler was added during a three minute mixing period which started after the last 30 minute reheating mentioned above. After mixing, the asphalt and mineral filler were immediately cast into beams.

<u>Aging</u>: High temperature accelerates the processes that cause aging in both asphalt and rubber. Researchers have taken advantage of this to simulate the long time effects of weathering in a relatively short period for laboratory work. This type of accelerated aging has been used for both asphalt and rubber. Such a procedure was used in this investigation for the study of aging of the various asphalts and rubber modified asphalts.

The asphalt was heated for one hour in an oven at $275^{\circ}F$; then poured into eleven inch by nineteen inch enameled steel trays. This resulted in a film of asphalt of approximately one eighth inch deep for the 400 gram specimens being aged. The trays were then placed into a thermostatically controlled oven which was maintained at $275^{\circ}F$ for 24 hours. Air was allowed to circulate around the aging specimen by open vents in the top and bottom of the oven. This cycle of 24 hours at $275^{\circ}F$ was selected after a study of previous work (33) indicated that a reasonable aging effect could be obtained at this relatively low temperature. A low temperature was considered desirable to eliminate the possibility of depolymerization of the rubbery second phase.

To determine if the changes in the rubber modified asphalt observed during the above aging cycle could be expected to occur at temperatures that are encountered in service; one series of beams was made of asphalt that had been aged for 10 days at 150°F.

<u>Testing</u>: The beams were tested in an Instron Testing Machine. A constant loading rate of 0.1 inch per minute was used for all tests. A plot of load versus deflection was obtained directly from the testing machine.

Since low temperatures were necessary, all testing was done inside an insulated chamber in which the low test temperatures could be maintained. Test temperatures were regulated by the use of liquid nitrogen and forced circulation of the air in the chamber. The test chamber is shown mounted on the cross arm of the testing machine in Figure 2.

The asphalt beams were kept at the test temperature at least 20 minutes before testing. This was found to be sufficient time to reach an equilibrium temperature since no difference in test results was obtained between beams cooled 20 minutes and beams cooled one hour.

<u>Computation of G_c :</u> After the beams had been tested to failure, the plotted data output was used to find E, and σ_n for each specimen. Then using the values of E and σ_n , G_c was computed.

The modulus of elasticity (E) for each type of team was determined from the force versus deflection plot of the testing machine for tests on unnotched beams. The deflection formula for simply supported beams loaded at midpoint was used.

-26-

$$Y = \frac{1}{48} \cdot \frac{PL}{EI}^{3}$$

Where P is the applied load, L is the span length, I is the moment of inertia of the beam and Y is the deflection of the midspan for a load P.

Solving for E gives:

$$E = \frac{PL^3}{48IY}$$

The normal bending stress at the root of the notch $\binom{\sigma}{n}$ was found from the flexure formula

$$n = \frac{M_b \cdot C_n}{I_n}$$

where M_b is the bending moment at the notched section at failure, C_n is one half of the depth of the unnotched portion of the beam, and I_n is the moment of inertia of the notched cross section.

After σ_n and E are known for a type of beam, their values can be substituted into equation number 7 to determine the critical strain energy release rate, G_c . The value of f(c/d) can be considered to be 0.47 for the depth of notch used in this study (18).

Sheet Asphalt

<u>Mix Preparation</u>: The asphalt and aggregate used for the sheet asphalt were heated in separate containers to $325^{\circ}F$ before mixing. The mixer bowl and paddle to be used were also heated to $325^{\circ}F$. The heated asphalt was weighed into the pre-weighed aggregate and mixed for one minute. The mixture was scraped from the sides of the bowl with a heated spatula and then

Eq. 9

Eq. 10

-27-

stored in a freezer at -10[°]C until used to make test cylinders. <u>Specimen Preparation</u>: A miniature Marshal Compaction Apparatus was used to make specimens from the prepared mix.

About 165 grains of sand asphalt mix were weighed and heated in an oven for 15 minutes at 275°F. The mix was then compacted into the steel molds which had also been previously heated. The molds were 1.4 inches in diameter and 3 inches long. The cylinders were compacted with medium compactive effort corresponding to medium traffic design category (ASTM). The compactive effort was scaled down for the smaller than standard specimens and the hammer used weighed 5.33 pounds and had a free fall of 10 inches. The compactive effort in foot pounds of energy to volume of specimen was maintained the same as for the full size Marshall Test. This was calculated to be 48 blows with the small hammer.

The predetermined weight of asphalt mixture was placed in the mold. The mixture was given one-half the number of hammer blows calculated for the amount of compaction desired, that is 24 out of 48 blows. Each blow delivered 4.45 ft.-lb. of energy. The specimen was then turned over and 24 compaction blows were given on the opposite end. The specimen was cooled for a short time and extruded from the mold by means of a special hydraulic jack apparatus, then brought to room temperature and stored in a refrigerator until ready for testing.

The bulk densities of the cylinders were determined by weighing the specimens in air and then in water. The expression used for bulk density of the specimens was:

 $D = \frac{\text{weight in air}}{\text{weight in air - weight in water}}$

-28-

It was found that the compaction procedure just stated yielded specimens that were uniform and of almost identical bulk densities for each type of mixture.

Testing: The cylinders were tested at -5° C and 25° C on an Instron Testing Machine. A triaxial test cell was mounted on the cross head of the testing machine. The test temperature was maintained by circulating cold water through the cell. A thermostatically controlled heater in the cell maintained the temperature to within $\pm 0.2^{\circ}$ C. At the -5° C test temperature, ethylene gycol was added to the circulating water to prevent freezing.

The test specimens were placed in the temperature controlled testing cell for one hour before testing. The specimens were preconditioned by compressing each cylinder 0.5% of its initial length at the rate of 0.1 inch per minute and removing the strain immediately. The preconditioning compression was repeated until there was very little change in load necessary to strain the specimen 0.5%. Three or four loadings were usually required to achieve repeatable results.

After preconditioning, the specimens remained unloaded for 10 minutes before testing. This allowed most of the deformation induced by the preconditioning to disappear. The specimens were then compressed at a loading rate of 0.02 inches per minute, to failure. The maximum load carried and the deformation at that load were obtained from the loaddeflection plot made by the testing machine.

Microscopic Study

The microscopic structures of the various rubber-asphalt mixtures were studied in order to learn if there were basic differences in the types of structures formed.

Samples were obtained by taking small amounts of asphalt from the center part of broken test beams with the

-29-

tip of a knife. The asphalt was placed on a microscopic slide and covered with a cover glass. The specimen was heated in an oven at 140° C for 10 minutes. The slide was then removed and the asphalt was pressed into a thin film by applying finger pressure to the cover glass. This resulted in a specimen that could easily be examined with transmitted light in an optical microscope.

VI: RESULTS AND DICUSSION

The results of the notched beam tests are given in this section. The discussion has been divided into sections to correspond with the various phases of the study. The values of modulus of elasticity (E) load to fracture for notched beams (Pm) and critical strain energy release rate (G_c) are summarized in tables in each section.

The results of the microscopic study are discussed and typical micrographs are included which show the variation in structure of the rubbery second phase in the asphalt.

Preliminary Results

Preliminary tests were run on specimens made of B-3056 or B-2960 asphalt and various rubbers to determine which asphalt-rubber combinations were the most promising for more detailed investigation. Table 3 summarizes the results of the preliminary tests.

Several of the combinations tested were substantially tougher than the unmodified asphalts. However, the L-170 latex gave the greatest increase of G_c of any of the rubbers tested when combined with either of the asphalts used.

The combination of CTBN and epoxy added to B-2960 also showed a significant increase of G_c during the preliminary testing.

During this preliminary testing, it was observed that there was an obvious correlation between the increase in fracture toughness as determined by the notched beam test and the consistency of the rubber modified asphalt at 140°C.

For the mixtures that showed a major increase in G_c over the unmodified asphalt, a rubbery gel-like structure formed after mixing. This rubbery consistency seemed to be relatively

-31-

insensitive to temperature and in some cases was thick enough to prevent pouring the asphalt into the molds at 140°C. At this temperature, unmodified asphalt is liquid enough to pour freely.

The preliminary testing also included a series of tests on various combinations and proportions of asphalt, CTBN, epoxy, and hardener. These combinations were mixed together in small quantities, and exposed to 140°C temperatures for different lengths of time. The consistency of the material was observed to determine to what degree, if any, the asphalt was forming the characteristic gel structure which indicates that the asphalt is being appreciably modified by the rubber.

As a result of these qualitative tests, it was concluded that it was necessary to add both epoxy and hardener to the asphalt-CTBN mixture to achieve the rubbery gel structure. Further, it appeared that a minimum of 30% epoxy and 10% DMP-30 (as a percent of CTBN) was necessary to obtain the reaction that produced the rubbery consistency.

To determine what effect the liquid CTBN alone had on the fracture toughness of asphalt, notched beam tests were run on mixtures of both B-2960 and CTBN and B-3056 and CTBN. No epoxy or hardener was used in these tests and no gel formation was observed. The results of the test showed no significant change in either the modulus of elasticity or fracture toughness of the asphalt at low temperatures.

Most of the notched beams tested in this study displayed a linear force-deformation curve to failure, failed catastrophically, and showed no macroscopic, residual deformation in the broken specimen. Since the usual criteria for brittle fracture was satisfied, the theory of brittle fracture could be applied to these specimens with assurance that the resulting critical strain energy release rate was a true material property.

Some of the specimens made of B-2960 asphalt modified with 4.5% rubber, particularily those aged before testing,

20

deviated from a brittle fracture mode and the crack did not propagate across the beam rapidly. The force deflection curve was linear almost to the point of maximum load, and no residual deformation could be detected. However, for these beams the calculated values of G_c were probably much larger than the actual values due to excessive, microscopic, plastic deformation which the specimen had undergone prior to failure.

Since these materials did not display a true brittle failure mode, the critical strain energy release rate computed may have been dependent on the geometry of the test specimen and the method of loading. Changing these conditions probably would result in different numerical results for G_c .

All the beams were tested under identical conditions of geometry and loading; so, although the tests on some of the tougher materials didn't result in a true material property, the values given are a reproducable measure of the relative toughness of the asphalts tested.

Effect of L-170

The addition of L-170 to B2960 produced significant increases in G_c at all three of the temperatures listed. Figure 3 illustrates the variation of G_c with the percent rubber added. The G_c values increase from 3 to 5 fold with the addition of 4.5% of L-170. The modulus of elasticity was decreased by 15% to 30% with the addition of 4.5% rubber. The load required to break the beams (Pm), however, was approximately doubled by the 4.5% addition. Table 4 summarizes the test results for modification of unaged B-2960 with L-170.

Even though the addition of L-170 increased the value of G_c significantly, an even more noticeable difference between the modified and unmodified asphalts can be seen in the shape of their respective load deflection curves. Typical load versus deflection curves for both modified and unmodified asphalt are shown in Figure 4.

-33-

The modified asphalt required a greater load to fail the beams, but the shape of the load versus deflection curve shows that the difference in work required to break the beams was much greater than the difference in either the maximum loads or the G_c values.

Effect of CTBN

Adding CTEN and epoxy to B-2960 increased the values of G_c substantially. Test values of G_c for 4.5% CTEN increased from 2 to 4 fold; Figure 5 shows how the values of G_c vary as the percent of CTEN is increased. The change in modulus of elasticity was about the same as for L-170 and the change in load at failure and G_c was slightly less. A summary of test results is given in Table 4.

Effect of Temperature

The variation in values of G_c with temperature is shown for typical tests in Figure 6. The values of G_c , for the various combinations tested, tended to increase gradually up to the glass transition temperature of the asphalt involved (-20^oF for B-2960). Above that point the values of G_c increased sharply for most of the test combinations.

The sharpest change in the slope of the line is somewhere near the original glass transition temperature for both modified and unmodified asphalts.

This indicated, in an approximate manner, that the glass transition temperature of the asphalt was not drastically changed by the introduction of the rubbery second phase.

Evelow the glass transition temperature the individual molecules of the asphalt are fixed with respect to one another and are not free to move. At these temperatures asphalt is a glassy solid with only a very limited capability for plastic flow. In this condition the work absorbed by plastic

-34-

flow in the specimen is limited and variations in temperatures have only limited effect on the fracture toughness.

As the temperature of the asphalt is raised above the glass transition temperature, the long chain molecules become free to move past one another and plastic flow becomes progressively easier. Above the glass transition temperature the work absorbed by plastic flow during fracture is the dominate factor in providing resistance to the advancing crack. Therefore, at temperatures above the glass transition the values of fracture toughness become more dependent on variations in the temperature.

Effect of Mineral Filler

The effects of adding 75% mineral filler to the rubber modified asphalts is summarized in Table 5.

The change in properties that was observed was generally the same whether the asphalt had been modified with L-170 or CTBN and epoxy.

The most noticeable changes were in the values of E and P_m . Both of these values were increased significantly. The modulus (E) was increased between 80% and 150% by the addition of the mineral filler and the load on the notched beams at failure (P_m) was increased between 20% and 70%.

However, the values of the critical strain energy release rate (G_c) displayed no consistent change as a result of the addition of the mineral filler. This contrasted with a previous study which found that G_c was increased substantially by the addition of mineral filler to unmodified asphalt (34). This difference in the effect of the mineral filler on modified and unmodified asphalt may be explained by the difference in the type of mechanism responsible for the toughening.

-35-

In the study which noted a marked increase in the values of G_c when mineral filler was added to asphalt; the suggested mechanism was the larger surface area created by the fracture compared to the area created by the fracture of pure asphalt.

It was suggested that this was a result of the advancing crack tip being forced to go around the individual mineral filler grains. This resulted in a rough, "grainy" fracture surface which was substantially larger in actual area than the glassy smooth surfaces created by the fracture of the pure asphalt beams.

Since the energy required to create new surfaces is proportional to the area of these surfaces it was reasonable to suggest that this increase in surface area was responsible for the increase in the value of G noted.

The toughening mechanism involved in the fracture of rubber modified asphalt is apparently not dependent on the increase of actual surface area created. The way the rubber modification increases the fracture toughness is not completely known; but a possible mechanism for this toughening is proposed in the section of microscopic work. The toughening mechanism of the rubber modification is apparently the dominate influence and the presence or absence of mineral filler has very little effect on the fracture toughness of modified asphalts.

The failure of the mineral filler to toughen the modified asphalt may be due to insufficient bonding between the matrix and filler. In impact-resistant thermoplastics, toughening agents have been found most effective when "interpolymerized" with the matrix. Failure to toughen due to lack of bonding has been noted when fine polyethylene particles were dispersed in epoxy and polyester matrices (36). A similar lack of sufficient bonding between the matrix and the dispersed

-36-

particles may prevent toughening in the asphalt and mineral filler.

Effect of Aging

The changes in G_c at $-20^{\circ}F$ obtained by aging the material in a thin film for 24 hours at $275^{\circ}F$ is shown in Figure 7. The general trend for unmodified asphalt was a decrease in G_c with aging for all test temperatures. The typical decrease of G_c was about 30%. In contrast, values of G_c increased during the aging cycle for the rubber modified asphalts.

The change in properties of asphalt modified with L-170 are summarized in Table 6. Modulus of elasticity, load at failure and G_c , all increased during aging. The range of increase in G_c was as high as 2.5 times the value before aging.

The change in properties during aging of asphalt modified with CTBN and epoxy are summarized in Table 7. The changes are generally similar to those of the L-170 modified asphalt.

Rubber deteriorates from the effects of heat and exposure to oxygen and over a period of time loses much of its original strength and flexibility. Asphalt is also adversly affected by exposure to heat and oxygen and normally becomes more brittle. This is illustrated by the values of G_c for unmodified asphalt found in this study. In all cases these were found to be lower after aging.

Since rubber and asphalt both normally tend to become more brittle when held at elevated temperatures for extended periods of time, the increase in fracture toughness during aging for combinations of these two materials was not expected.

This unexpected increase in the fracture toughness of rubber modified asphalt during aging is apparently a result of changes in the rubbery second phase caused by prolonged exposure to high temperature and may involve the following

-37-

mechanisms.

Rubber swells and disolves in asphalt at high temperatures (28,29). This results in a wider dispersion of the rubber. The results of this wider dispersion is a finer network of second phase material that may be responsible for the increase in toughness during aging. This is supported by microscopic study of the rubber modified asphalts which indicate that there is a correlation between the fracture toughness and the fineness of the "network" of the second phase. This is more fully discussed in the second on microscopic work.

Curing of the rubber may be another mechanism possible for the increase in fracture toughness with aging. The rubber in the L-170 latex is a virgin, uncured rubber when mixed into the asphalt. The prolonged exposure to high temperature in the asphalt may encourage partial curing or vulcinizing of the rubber into a stiffer material thus changing the properties of the asphalt-rubber combination. This reaction may be encouraged by small amounts of sulfur in the asphalt which would encourage the curing or vulcanizing reaction.

A similar explanation may account for the increase of G_c during aging of the CTBN-epoxy modified asphalt. The epoxy and hardener added to the hot asphalt containing CTBN causes the liquid rubber to polymerize into longer chain molecules, and form cross links between these molecules. The effect of this polymerization and cross-linking is that the material changes from a liquid to a rubbery form.

Holding this combination of material at high temperature for long periods of time probably allows the polymerizationcross-linking reaction to proceed further with an increase in the stiffness of the material.

This explanation would satisfactorily account for the increase in G_c since the increase during aging is due to an increase in the maximum load supported by the notched beams. not by a reduction in modulus. The modulus actually increases

-38-

slightly during aging.

This unexpected increase in fracture toughness during aging suggests that the potential for toughening asphalt with rubber may be much greater than achieved during this study. The values of G_c for modified asphalt increased up to 2.5 times during the aging process used for the study (24 hours at 275°F). It may be possible to achieve much greater increases in toughness by optimizing the temperature and time of processing. Conversely, it may be possible to reach the level of toughening measured during this study by using smaller percentages of rubber thus reducing the cost of the modification.

Although the toughening of the modified asphalts during aging suggests the possibility of more effective modification; this phenomenon complicated the attempt to determine if rubber modification enhances the asphalt's resistance to aging under actual field conditions.

The aging procedure used (24 hours at $275^{\circ}F$) reduced the toughness of unmodified asphalt a significant amount, indicating that it was reasonably well related to actual aging where asphalts are known to become more brittle with time. However, it was not known if the $275^{\circ}F$ temperature used causes changes in the modified asphalts which might not occur at the temperatures reached in actual use.

To see if these changes would also take place at lower temperatures, a series of tests were run on beams of B-2960 which had been modified with 4.5% L-170 and held at 150° F for 10 days.

The values of G_c computed from these tests were also greater than the values of G_c for unaged material. This increase in toughness during aging at 150°F indicated that

-39-

such change could reasonably be expected to take place during actual use where the material is exposed to similar temperatures.

It therefore seems reasonable to expect that rubber modification will reduce the deterioration of which normally occurs during its service life.

Sheet Asphalt

The results of the compressive tests on the sheet asphalt mixtures are given in Table 8.

The compressive stress at failure for the cylinders made of rubber modified asphalt was between 13% and 43% less than the stress at failure for the cylinders made of the unmodified asphalt. The deformation of the cylinders at maximum load was approximately twice as much for the mixtures containing rubber.

The loss in strength at $-5^{\circ}C$ is not considered to be important since the strength levels of asphaltic pavements at low temperatures are much higher than needed to support the traffic load. The additional deformation possible before failure of the modified mixes should help the pavement structure adjust to deformations caused by thermal stress or base movement.

The loss in strength found at 25° C may be a shortcoming if substantiated by future testing; however, it should be noted that this loss was only 13% for the sheet asphalt modified with 4.5% L-170.

A review of the densities of the test cylinders reveals a condition which may account for part or all of the difference in strengths of modified and unmodified sheet asphalt. The mixtures made of modified sheet asphalt were less dense than the plain asphalt mixtures. Since identical compactive effort was used, the mixture containing rubber was apparently more difficult to compact, at least with the impact type compaction

-40-

used. This less dense condition probably was a major reason for the lower compressive strength of the rubber modified mixture.

Microscopic Study

The microscopic study gave some insight into the form of the rubber or rubber-asphalt mixture that formed the second phase in the modified asphalt. The second phase, which usually appeared in the microscope as a white network-like area, appeared to occupy much more space than seemed possible for the small percentage of rubber involved. For this reason, it is believed that the second phase is a combination of rubber and an asphalt component within a relatively pure asphalt mitrix.

There seemed to be a relationship between the form of the second phase as observed by optical microscopy and the fracture toughness of the material. It was noted that the combinations which appeared to have finer dispersions of the rubbery second phase also usually had higher values of G_c when tested. This was true between specimens modified with different types of rubber as well as between specimens involving the same type of rubbers but with different dispersions because of aging.

This relationship can be seen by comparing the pictures in Figures 8 and 9 with the G_c values given in Tables 6 and 7.

The most striking difference noted in the specimens was the difference between the aged and unaged asphalt. The aged asphalt consistantly had a more finely dispersed second phase. This paralleled the test values of G_c which also were consistantly higher for aged asphalts.

A marked difference was also noted between the L-170 and CTBN modifications before aging; with the L-170 producing a finer dispersion and higher values of G_c in all but a few cases.

-41-

After aging however, it was more difficult to determine which rubber produced the finer dispersion. The second phases were different in appearance but seemed to be about equally well dispersed. This again agreed reasonably well with the results of the notched beam tests since no constant superiority in fracture toughness could be found between L-170 and CTEN modifications after aging.

This correlation between the fineness of the second phase and the values of G_c parallels the relationship noted earlier between the consistency of the asphalt and the values of G_c . The increase in G_c seemed to correspond to the formation of a gel-like structure in the asphalt and rough estimates of the fracture toughness could be made based on the difficulty of pouring the material at 140°C. These two visual guides may be helpful in further laboratory work or for use as indicator tests for control of construction.

The structure of the rubbery second phase observed in the modified asphalt suggests that the toughening mechanism of the asphalt may be different from the mechanism responsible for the toughening of brittle plastics described earlier. To effectively toughen plastics the rubbery second phase is discontinuously dispersed throughout the matrix in the form of very small spheres. The toughening is explained as a result of a relatively large volume of the matrix being plastically deformed by the stress concentrations around the inclusions.

Although the rubbery second phase in the asphalt is in the form of a network instead of discontinuous particles, it seems likely that the dispersion of the low modulus rubber through the asphalt also causes a non-uniform stress field. It also seems reasonable that asphalt in the areas of high stress concentrations may flow plastically on a microscopic level and thus involve a large

-42-

volume of the matrix in energy absorbing plastic flow before fracture occurs.

However, the large volume of the rubber-asphalt second phase coupled with its continuous nature suggests that the crack inhibitor theory may help explain the toughening of the rubber modified asphalt. The relative strengths of the second phase and the matrix also support this explanation.

Unmodified asphalt has only a small fraction of the strength of the unmodified plastics discussed earlier. Therefore, it is more likely that the rubbery second phase has a significant effect as a crack inhibitor in asphalt since the stress levels involved are much lower.

No conclusions were reached about the exact nature of this modification as a result of the limited microscopic work done during this study. Additional experimental work will be necessary to reliably determine the toughening mechanism of the asphalt.

Cost Comparisons

In considering the use of an unconventional engineering material, the anticipated advantages must be balanced against the additional cost.

The amount of improvement that can be expected from rubber modification of asphaltic paving materials is not known; however, the test results of this study suggest that substantial improvement in resistance to aging and cracking may be possible.

The additional cost of rubber modified asphalt over conventional asphalt is easier to estimate than the expected improvement. Rubber has been used in asphalt without special construction equipment and without unusual

-43-

difficulties (28, 29). Although there may be additional expenses involved in providing additional storage and mixing equipment at the plant, these would be only a relatively small addition to the equipment already required. It is expected that the extra cost of the rubber modification should be almost entirely dependent on the cost of the additional material.

The cost of these additional materials for an asphaltic concrete containing 6% of an asphalt modified with 4.5% rubber is computed below:

Weight of Rubber Required per Ton of Mix:

2000 lbs/T. x 0.06 x 0.045 = 5.4 lbs/T. Estimated Prices:

L-170	\$0.45/1b.
CTBN	\$0.50/1b.
Epoxy (Epon 828)	\$0.70/lb.
Hardener (DMP-30)	\$0.50/1b.

Material Costs for Modification with 4.5% L-170: Cost of L-170 = 5.4 lbs/T. x 0.45 % lb. = %2.43/T.

Material Costs for Modification with 4.5% CTBN, 1.5% Epoxy and 0.5% Hardener:

 Cost of CTBN
 =5.4 lbs/T. x 0.5. \$/lb.=\$2.70/T.

 Cost of Epoxy
 =1.8 lbs/T. x 0.70 \$/lb.=\$1.26/T.

 Cost of Hardener
 =0.6 lbs/T. x 2.50 \$/lb.=\$1.50/T.

 Total Cost for CTBN Modification
 =\$5.46/T.

The cost of asphalic concrete varies over a wide range depending on location, construction conditions, quantity placed etc. A typical price for an average paving project is \$12.00 per ton including the cost of placement. Since the rubber modification is not expected to make construction significantly more difficult, the additional cost for modification with 4.5% L-170 would represent an increase in cost of approximately 20%. The cost for modification with 4.5% CTBN would be approximately 40% over the cost of unmodified asphaltic concrete.

In order to justify the use of CTBN in the proportions used in this study, a major increase in performance would have to be achieved. However, use of L-170 might be justified by a more modest improvement in performance.

Modification of asphalt can be justified by either an increase in the service life or a reduction in the amount of paving material required for a particular design level. It can easily be seen that an increase in the usuable service life before resurfacing from ten years to twelve years, or a decrease in the required thickness of surface course from 2 1/2 inches to 2 inches are examples of improvements that would result in sufficient savings to justify the use of 4.5% L-170 as a modifier.

This study did not attempt to predict performance characteristics of modified asphalt paving mixtures. However, the substantial improvement in fracture toughness which was found indicates that major improvement in resistance to aging and cracking may be obtainable. If subsequent tests confirm that these inprovements are possible, rubber modified asphalt may offer a superior, more economical paving material.

-45-

VII: CONCLUSIONS

On the basis of this study the following conclusions appear valid:

1. Fracture toughness of asphalt as measured by the notched beam test can be increased substantially by addition of a suitable rubber as a latex or as a low molecular weight liquid which can be cross-linked into a rubbery solid after mixing with the asphalt.

2. Major increase in the fracture toughness can be achieved by holding the mixture at elevated temperatures for 24 hours.

3. Mixing mineral filler with rubber modified asphalt results in a binder that has higher flexure strength but which shows no increase in fracture toughness as measured by the critical strain energy release rate.

4. Rubber modified asphalt does not become brittle during accelerated aging as is normal for unmodified asphalt.

5. The deformation before failure of modified sheet asphalt was approximately twice the deformation of comparable unmodified material. This increase is expected to reduce cracking by allowing the mixture to better conform to deformations in the base and to thermal volume changes. The increase in allowable deformation was accompanied by a lower unconfined compressive strength although this was most noticeable at low temperatures where strength is not a critical factor.

6. Since the results of this study indicate that rubber modification may improve the performance of asphalt both in resistance to cracking and resistance to aging it is suggested that the following study may be of value.

-46-

- A. Optimization of the modification procedure with special emphasis on the effects of prolonged heating. This could be especially beneficial for modification with CTBN and epoxy since there are several variables and this study did not thoroughly investigate the effect of proportioning the individual components.
- B. Additional tests on the effects of rubber modification on asphalt-aggregate mixtures to determine if modification will result in improved performance of the paving mixture.

LIST OF REFERENCES

REFERENCES

- Moavenzadeh, F., "Asphalt Fracture", <u>Proceedings</u>, <u>Association of Asphalt Paving Technologists</u>, Vol. 36, 1967, pp. 51-79.
- Winters, Walter F., "Barytes in Rubber-Asphalt Mixtures", <u>Proceedings, Association of Asphalt Paving Technologists</u>, Vol. 25, 1956, pp. 379-391.
- 3. Thompson, Donald C., "Rubber Modifiers", p. 375, in <u>Bituminous Materials: Asphalt, Tars, and Pitches</u>, ed. by Arnold J. Hoiberg, New York, Interscience Publishers 1964.
- 4. Thompson, Donald C., and Hagman, J.F., "The Modification of Asphalt with Neoprene", <u>Proceedings</u>, <u>Association of</u> Asphalt Paving Technologists, Vol. 27, 1958, pp. 494-518.
- 5. Rice, James J., "Field and Laboratory Experience with Natural Rubber as an Additive for Asphalt", unpublished report represented at the Asphalt Insitute Symposium on Rubber in Asphalt, Chicago, March 24, 1960.
- 6. Gregg, L.E., and Alcoke, W.F., "Investigations of Rubber Additives in Asphalt Paving Mixtures," <u>Proceedings</u>, <u>Association of Asphalt Paving Technologists</u>, Vol. 23, 1954.
- Mack, Charles, "Physical Aspects of Hardening on Paving Asphalts", <u>Proceedings, Association of Asphalt Paving</u> Technologists, Vol. 27, 1958, pp. 183.
- Mack, Charles, "An Appraisal of Failure in Bituminous Pavements", <u>Proceedings, Association of Asphalt Paving</u> <u>Technologists</u>, Vol. 34, 1965, p. 234.

-49-

- 9. Doyle, Phil C., "Cracking Characteristics of Asphaltic Cement", Proceedings, Association of Asphalt Paving <u>Technologists</u>, Vol. 27, 1958, p. 581.
- 10. Marker, Vaughn, "Introductory Statement", <u>Proceedings</u>, <u>Association of Asphalt Paving Technologists</u>, Vol. 35, 1966, pp. 239-247.
- 11. Monismith, Carl L., "Flexibility Characteristics of Asphaltic Paving Mixtures", Proceedings, Association of Paving Technologists, Vol. 27, 1958, pp. 74-106.
- 12. Schmidt, R.J., "The Relationship of the Low Temperature Maximum Deformability of Asphalt to the Cracking of Pavements", <u>Proceedings</u>, Association of Asphalt Paving <u>Technologists</u>, Vol. 35, 1966, p. 263.
- Hughes, E.C. and Faris, R. B., Jr., "Low Temperature Maximum Deformability of Asphalts", <u>Proceedings, Association</u> of Asphalt Paving Technologists, Vol. 19, 1950, p. 329.
- 14. Griffith, A.A., "The Phenomena of Rupture and Flow in Solids", <u>Philosophical Transactions</u>, Royal Society of London, Series A, Vol. 221, 1920.
- 15. Griffith, A.A., "The Theory of Rupture", <u>First International</u> Congress of Applied Mechanics, Delft, 1929.
- 16. Irwin, G.R., "Relation of Stresses Near a Crack to the Crack Extension Force", <u>Proceedings Ninth International</u> <u>Congress of Applied Mechanics</u>, Paper No. 101 (11), Brussels, 1956.
- Irwin, G.R., "Fracture Mechanics", <u>First Symposium on</u> <u>Naval Structural Mechanics</u>, Stanford University, August, 1958.
- Kaplan, M.F., "Crack Propagation and the Fracture of Concrete", <u>Proceedings</u>, Journal of the American Concrete Institute, Vol. 58, Nov. 1961.

-50-

- Winnie, D.H., and Winndt, B.M., "Application of the Griffith-Irwin Theory of Crack Propagation to the Bursting Behavior of Discs, Including Analytical and Experimental Studies", Transactions, ASME, Vol. 80. 1958.
- 20. Berry, J.P. "Brittle Behavior of Polymeric Solids", <u>Fracture Processes in Polymeric Solids</u>, Interscience, New York, 1964
- 21. Broutman, L.J. and McGarry, F.J., "Fracture Surface Work Measurements on Glassy Polymers by a Cleavage Technique." "Effects of Temperature", Journal of Applied Polymer Science. Vol. 9, p. 589-608, (1965).
- 22. Willner, A.M., <u>Toughening of an Epoxy Resin by an Elastomeric</u> Second Phase, PhD Thesis, MIT, 1968.
- 23. McCarry, F.J., Willner, A.M. and Sultan, J.N., "Relationships Between Resin Fracture and Composite Properties", <u>Air</u> <u>Force Materials Laboratory Technical Report</u>, AFML-TR-67-381, December 1967.
- 24. Nielsen, L.E., <u>Mechanical Properties of Polymers</u>, Reinhold Publishing Co., New York (1962).
- 25. Bucknall, C.B., and Smith, R.R., "Stress-Whitening in High Impact Polystyrene", Polymer, p. 437-446, August 1965.
- 26. Welborn, J. York, and Babashak, John F. Jr., "A New Rubberized Asphalt for Roads", Journal of Highway Division, Proceedings Paper 1651, May 1958.
- 27. Highway Research Board Committee MCA3 progress report on <u>Bituminous Surface Treatments with Modified Binders</u>, 1963-1964.
- 28. Benson, Jewell R., "New Concepts in Rubberized Asphalts", Roads and Streets, Vol. 28, No. 4, April 1955, pp. 37-44.
- 29. MacDonald, Charles H., "A New Patching Material for Pavement Failures", <u>Highway Research Record</u> No. 146, pp. 1-16, 1966.

- 30. Rex, H.M., and Peck, R.A., "A Laboratory Study of Asphalt Paving Materials", Public Roads, Vol. 28, No. 4, Oct. 1954.
- 31. Clinebell, B.J., and Straka, L.E., <u>A Survey on the Use</u> of Rubber in Bituminous Pavements: 1945-1951, Reprint, The Rubber Age, New York, October 1951.
- 32. Schmidt, R.J. and J. Santucci, L.E., "A Practical Method for Determining the Glass Transition Temperature of Asphalts and Calculation of Their Low Temperature Viscosites", <u>Proceedings, Association of Asphalt Paving</u> <u>Technologists</u>, Vol. 35, 1966, p. 61.
- 33. Moavenzadeh. Fred and Stander, R.R., <u>Durability</u> <u>Characteristics of Asphalt Materials</u>, Report No. EES 259-1, Ohio State University, Columbus, Ohio, June 1966.
- 34. Kakel, William W., <u>Fracture in Asphaltic Mixtures</u>, S.M. Thesis, MIT, 1968.
- 35. Tech-Book Facts, Technical Bulletin, Methods, pp. 2, Goodyear Chemical Division, Goodyear Tire and Rubber Co.
- 36. McGarry, F.J. and Stegeman, F.C., "Relationships Between Resin Fracture and Composite Properties. Crack Propagation Behavior of Thermoset Resins Containing Polyethylene Microparticles", <u>First Quarterly Report</u>, Contract AF33(615)-2712 to Air Force Materials Laboratory, Wright Patterson Air Force Base (September 1965).

-52-

ASPHALT	ADDITIVE	E 10 ⁻⁷ DYNES/CM ²	p max 10 ⁻⁵ dynes	Gc 10 ⁻⁴ ERGS/CM ²
	none	670	3.6	0.2
	2508	760	7.6	0.8
B-3 056	2518	860	9.3	0.9
B-3090	L-170	720	9.8	1.4
	CTBN	828	4.4	0.2
	CTBN+Epoxy	655	4.0	0.2
	none	386	5.8	0.9
	L- 170	350	10.2	3.0
в-2960	Nat. Rubber	334	8.9	2.5
	CTBN	3 78	4.4	0.5
	CTBN+Epoxy	365	8.9	2.3

TABLE 3 : Data Summary of Preliminary Tests of Unaged Asphalts Modified with 5% Rubber and 0% Mineral Filler.

Si Cu

TYPE OF RUBBER	TEMP. (°F)	% RUBBER	10 ⁷ DYNES PER CM ²	P MAX. 105 DYNES	10 ⁴ Gc 10 ⁴ ERGS PER CM ²
		· 0	267	5.8	1.3
	-10	3			
			192	5.8	1.3
		4.5	183	8.2	3.8
L-170		3	<u> </u>	<u> </u>	0.9
	-20				1.2
	-30	4.5	305	<u> </u>	<u> </u>
		3	<u> </u>	7.5	1.0
4		4.5	482	12.0	3.0
	f	- 4 • 0	267	5.8	1.3
	-10	3	256	8.0	2.5
	-10	4.5	174	9.3	5.1
			386	<u> </u>	0.9
CTBN	-20	3	430	6.7	1.1
		4.5	369	8,0	1.8
		0	590	5,8	0.6
	-30	3	690	5.3	0.4
	-	4.5	534	9.8	1.8

TABLE 4 : Data Summary for Unaged B-2960 Modified with Various Percentages of Rubber.

TEMP. (°F)	ADDITIVE	MINERAL FILLER (%)	10 ⁷ DYNES/ CM ²	P MAX 10 ⁵ DYNES	Gc 10 ⁴ ERGS/ CM ²
	No Rubber	0	267	5.8	1.3
	4.5% L-170	0	183	8.0	3.8
-10	4.5% L-170	75	495	13.3	3.7
	4.5% CTBN	0	174	9.3	
	4.5% CTBN	75	445	13.3	4.0
	No Rubber	0	386	5.8	0.9
	4.5% L-170	0	305	10.2	3.0
-20	4.5% L-170		760	14.6	
	4.5% CTBN	0	369	8.0	1.8
	4.5% CTBN		686	13.3	2.6
	No Rubber	0	590	5.8	0.6
-30	4.5% L-170	0	482	12.0	3.0
	4.5% L-170	75	875	14.2	2.3
	4.5% CTBN	0	534	9.8	1.8
	4.5% CTBN	75	970	13.3	1.9

TABLE 5 : Results of Tests on Modified and Unmodified B-2960 both with and without Mineral Filler.

-55-

ADDITIVE	AGING AT 275°F	TEMP. °F	e 10 ⁷ dynes per cm ²	p max 10 ⁵ dynes	Gc 10 ⁴ ERGS PER CM ²
		-10	267	5.8	1.3
	Unaged	-20	386	5.8	0.9
No Rubb er	0	-30	590	5.8	0.6
Rubber		-10	336	3.6	0,9
	24 Hrs.	-20	552	5.3	0.5
		-30	562	5.3	0.5
		-10	192	5.8	1.8
	Unaged	-20	367	6.7	1.2
3.0% L-170		- 30	603	7.5	1.0
		-10	334	8,0	1.9
	24 Hrs.	-20	370	7.1	1.4
		-30	<u>560</u>	8.4	1.3
		-10	183	8.2	3.8
	Unaged	-20	305	10.2	3.0
4.5%		-30	482	12.0	3.0
L-170		-10	226	7.6	2.6
	24 Hrs.	-20	355	16.4	7.7
		-30	594	19.0	6 .0

TABLE 6: Data Summary for Aged B-2960 Asphalt Modified with L-170 Rubber.

-56-

ADDITIVE	AGING AT 275°F	TEMP. °F	10 ⁷ E 10 ⁷ DYNES	P MAX 105 DYNES	10 ⁴ ERGS. PER CM ²
		-10	267	5.8	1.3 0.9
	UNAGED	-20	386	5.8	
NO		-30	590	5.8 5.8	0.6
RUBBER		-10	336	3.6	0.9
	24 HR.	-20	552	5.3	0.5
		-30	562	5.3	0.5
		-10	112	5.7	3.0
	UNAGED	-20	349	4.4	0.6
3.0%		-30	490	4.0	0.4
CTBN		-10	216	8.4	3.3
	24 HR.	-20	480	8.0	1.4
		-30	723	9.8	1.4
		-10	174	9.3	5.1
	UNAGED	-20	369	8.0	1.8
4.5% CTBN		-30	534	9.8	1.8
		-10	238	8.9	3.3
	24 HR.	-20	378	8.9	2.1
		-30	613	11.6	2.3

TABLE 7 : Data Summary for Aged B-2960 Asphalt Modified with CTBN and Epoxy.

TEST TEMP. °C	ADDITIVE	MAXIMUM LOAD (POUNDS)	MAXIMUM STRESS (PSI)	DEFORMATION AT MAX. LOAD (INCHES)
	No Rubber	2300	1450	0.060
-5°C	4.5% L-170	1495	970	0.136
	4.5% CTBN	1500	973	0.138
	No Rubber	212	135	0.045
	4.5% L-170		117	0.046
25°C	4.5% CTBN	118	77	0.124

TABLE 8 : Data Summary for Compressive Tests on Sheet Asphalt Cylinders. Loading Rate = 0.02"/min.

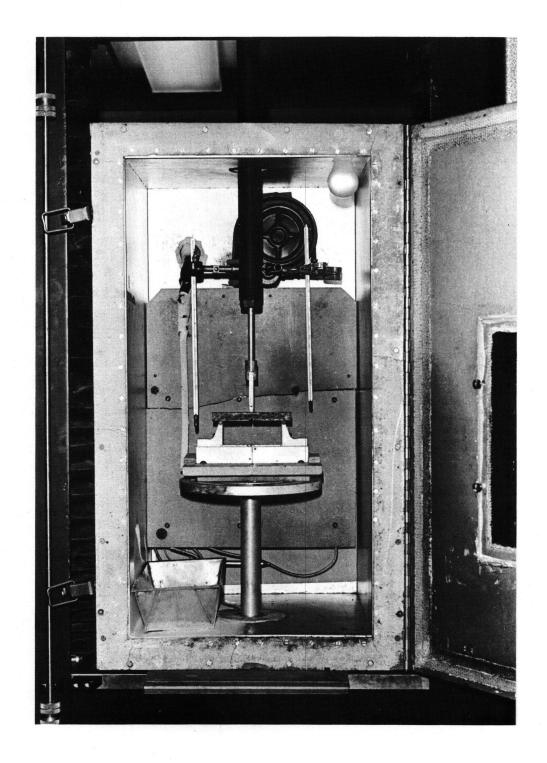
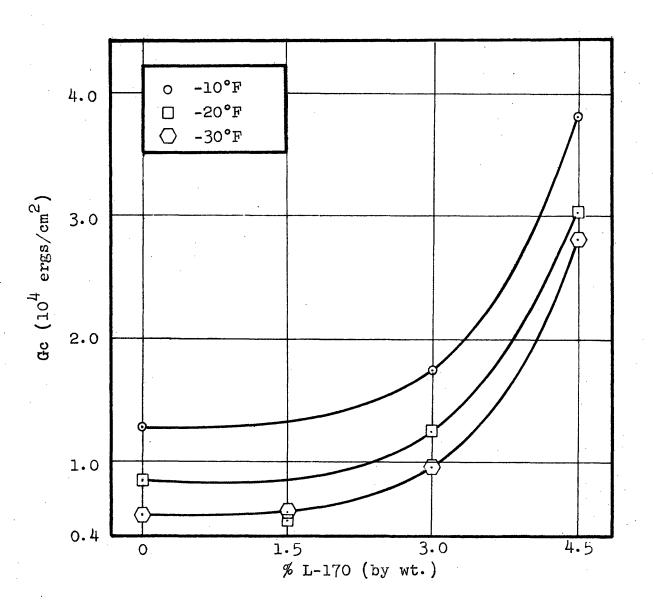
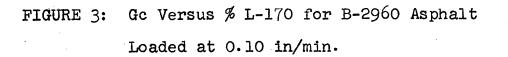
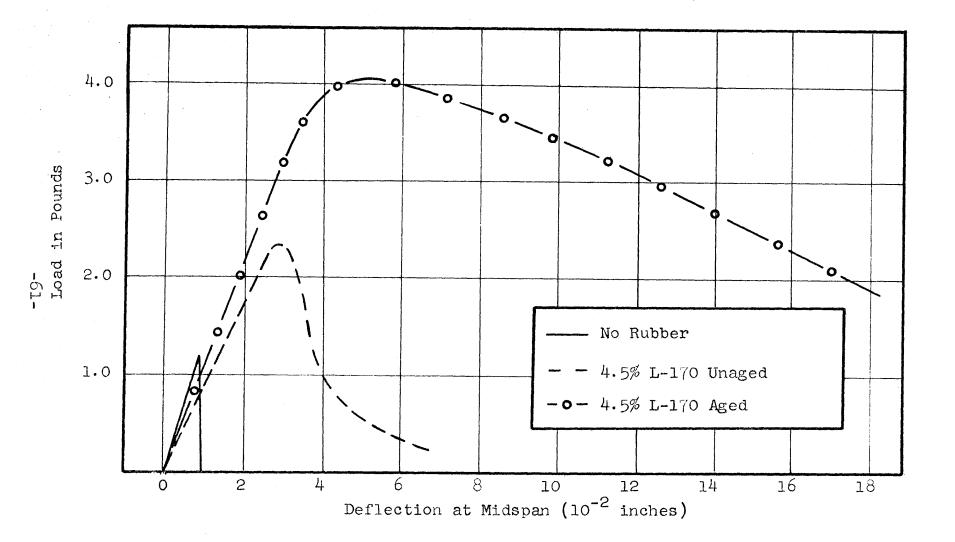
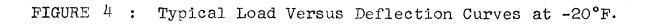


FIGURE 2: Apparatus for Testing Beams at Low Temperatures.









.

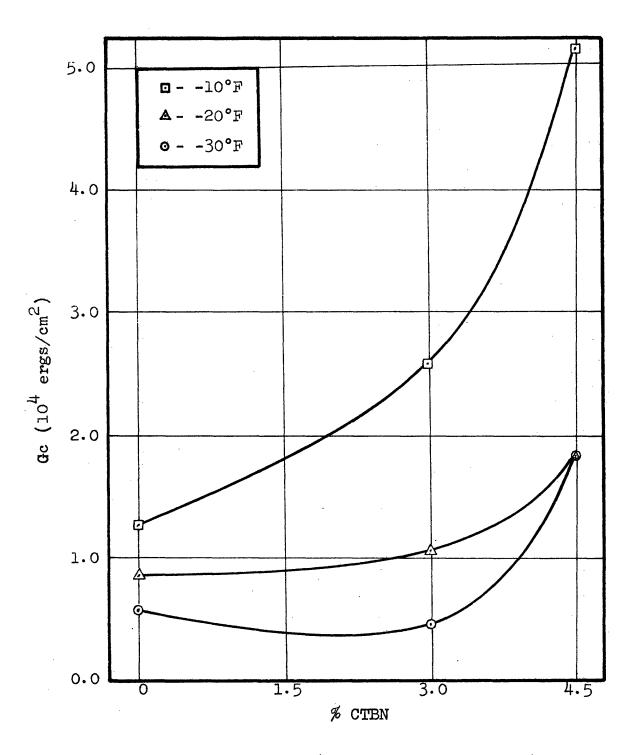


FIGURE 5: Gc Versus % CTBN for Unaged B-2960 Loaded at 0.10 in/min.

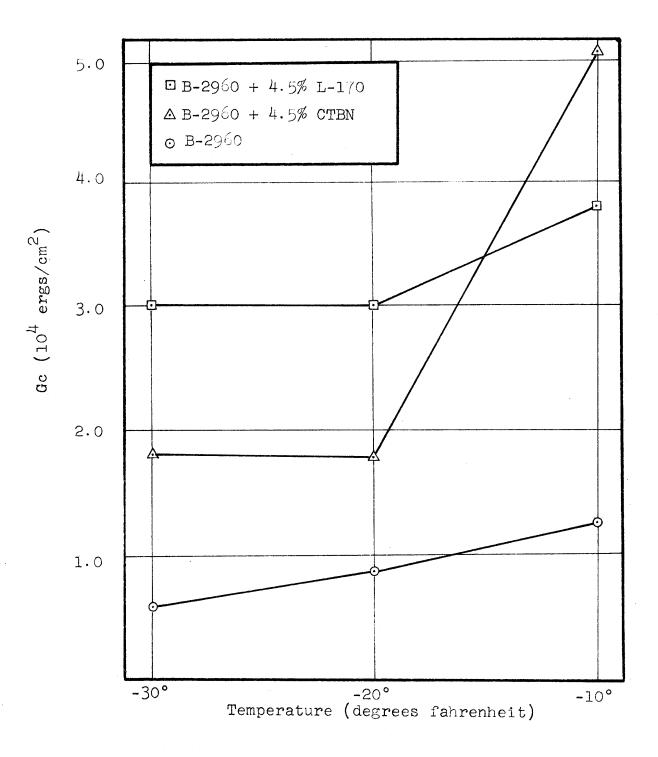
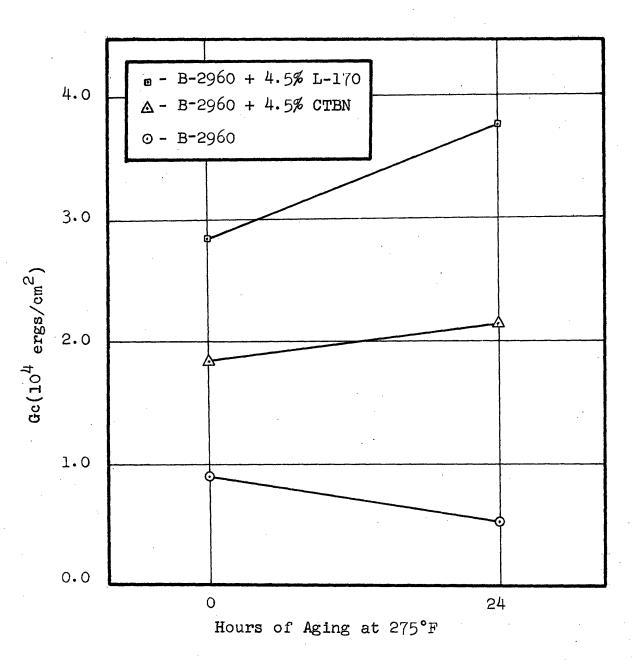
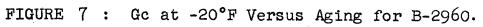
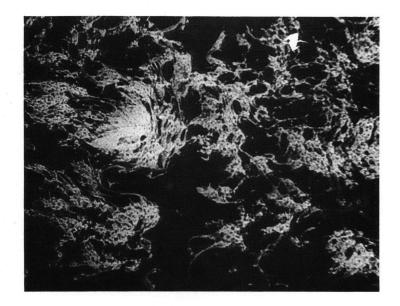


FIGURE 6 : Gc versus Temperature for B-2960.

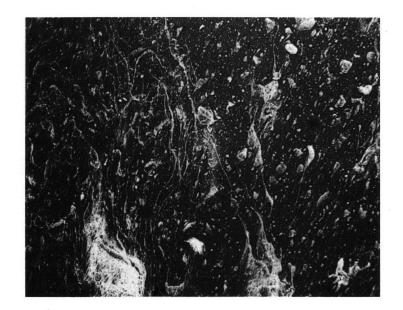




-64-

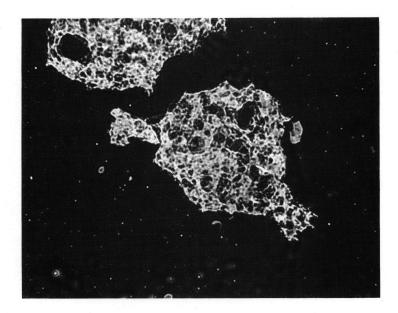


Before Aging

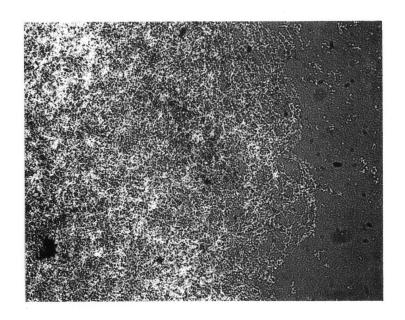


After Aging 24 Hours at 275°F

FIGURE 8: B-2960 Modified with 4.5% L-170, Before and After Aging (100X).



Before Aging



After Aging 24 Hours at 275°F

FIGURE 9: B-2960 Modified with 3% CTBN, Before and After Aging (100X).

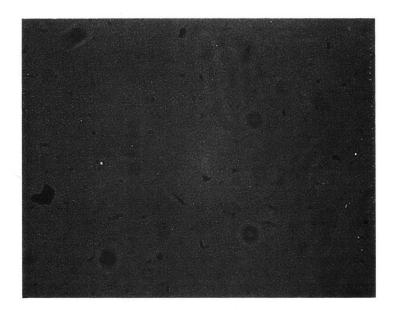


FIGURE 10: Unmodified B-2960 Asphalt at 100X.

APPENDICES

DEFINITION OF SYMBOLS

G	. =	strain-energy release rate
G _c	=	critical strain-energy release rate
c	=	length of crack (notch depth)
U	=	elastic strain energy of a system
σ	=	stress
E	=	modulus of elasticity
Т	=	energy required for the formation of the fracture surfaces of a system
γ	· =	surface energy of the material per unit area
W	=	T - U
μ	=	Poisson's ratio
ď	=	depth of beam
h	=	net depth of beam at notch (d-c)
L	=	span length
Р	=	applied load
P _m	=	load required to fracture a notched specimen
T g	=	glass transition temperature
Ý	=	deflection at midspan
I	=	moment of inertia of beam
In	=	moment of inertia of notched section of beam
σ _n	=	nominal stress at the crack tip
Mb	=	bending moment at notched section
c _n	=	one the depth of the unnotched portion of the beam (1/2 h)
D	=	bulk density of compacted sheet asphalt

-69-

LIST OF TABLES

<u> Table</u>		Page
1	Results of Typical Tests on Asphalt Used in this Study.	19
2	Gradation of Aggregate Used in Sheet Asphalt.	22
رن ا	Data Summary of Preliminary Tests of Unaged Asphalts Modified with 5% Rubber and 0% Mineral Filler.	53
4	Data Summary for Unaged B-2960 Modified with Various Percentages of Rubber	54
5	Results of Tests on Modified and Unmodified B-2960 Both with and without Mineral Filler.	55
6	Data Summary for Aged B-2960 Modified with L-170 Rubber.	56
7	Data Summary for Aged B-2960 Modified with CTBN and Epoxy.	57
8	Data Summary for Compressive Tests on Sheet Asphalt Cylinders Loading Rate = 0.002 in/mi	58 n.

LIST OF FIGURES

Figure		Page
1	Beam Geometry and Method of Loading	23
2	Apparatus for Testing Beams at Low Temperature	59
3	G versus % L-170 for unaged B-2960 loaded cat 0.10 in/min.	60
4	Typical Load versus Deflection Curves at -20 ⁰ F	61
5	G versus % CTEN for unaged E-2960 loaded at °0.10 in/min.	62
6	G _c versus Temperature for B-2960	63
7	G at -20 ⁰ versus aging for B-2960 and for CB-2960 Modified with L-170 and with CTBN	64
8	B-2960 Modified with 4.5% L-170, Before and After Aging (100X).	65
9	B-2960 Modified with 3% CTBN, Before and After Aging (100X).	66
10	Unmodified B-2960 Asphalt at 100X.	67

-71-