

Polyethylene-Modified Bitumen for Paving Applications

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Synopsis

In cold regions, transverse cracking of asphaltic paving materials is a serious problem which has not been completely resolved despite much effort. In this investigation, the low temperature stress-strain properties of bitumen containing dispersed polyethylene were measured over the temperature range from -40 to 0°C and compared with unmodified bitumen in an attempt to develop a tougher, more ductile crack-resistant binder for paving materials. Several grades of polyethylene were individually dispersed in liquid, heated bitumen to produce therein colloidal suspensions of polyethylene. The viscosities of these suspensions were determined at various temperatures and concentrations for each grade of polyethylene. Despite rather large differences in composition, molecular weight, and crystallinity of the polyethylenes, the differences in viscosity at the same concentration were relatively minor. However, the viscosity was very sensitive to the polyethylene concentration and the mixture became difficult to process at concentrations greater than 10 percent by weight. These hot mixtures were then cast into rectangular beams for flexural testing at temperatures below zero degrees Celsius. Near the optimum polyethylene concentration of 8 percent by weight, the bitumen mixture possessed increased flexural strength, increased flexural modulus, increased elongation, and increased fracture energy at temperatures near -30°C . In one example the energy to fracture was increased ninefold compared to a standard 80/100 pen. bitumen control at -20°C . Mix design results are presented for a typical aggregate and compared with a MTC HL4 hot-mix paving formulation which is used extensively throughout Ontario. The polyethylene-modified asphalt concrete mix displayed a curious increase in both the Marshall flow and the Marshall stability values. Dynamic mechanical measurements confirmed the expected increase in resilient modulus at temperatures above zero degrees Celsius. The Marshall briquets containing polyethylene also exhibited slightly greater wet strength retention after prolonged immersion in water. These observations are consistent with the published data for commercial Novophalt paving materials developed in Austria and predict that the use of polyethylene in asphaltic hot-mix paving materials can extend service temperature range at both high and low temperatures, thereby simultaneously reducing both pavement distortion (rutting) and low-temperature cracking, so that pavement lifetimes can be more than doubled. The cost of such modification can be substantially reduced if scrap or reclaim polyethylene is employed instead of virgin polyethylene. Dispersing agents, such as Shell Chemical Kraton G block copolymers were advantageously employed to control the emulsion stability, particle size, and compatibility of the dispersed polyethylene phase.

INTRODUCTION

In the design of asphalt paving surfaces for roads and highways, engineers are usually forced to compromise between mixes that are tough and resistant to cracking at low temperature extremes during winter seasons while also providing adequate pavement stability during hot summer periods so that creep and distortion due to traffic are minimized.¹⁻⁴ No single bitumen is capable of providing all the desired properties, particularly when subjected to large traffic densities and high axle loadings over extremes of

temperature. It has been established that low-temperature cracking of asphalt pavements is related to several factors, including the brittle temperature of the bitumen binder, the temperature gradient and the rate of cooling, thermal cycling, nature of the supporting base, age of the pavement, stress relaxation, creep rupture stress, and ultimate strain.³ Once a crack has been initiated, the intrusion of water can accelerate deterioration and reduce the service life of the pavement. At elevated temperatures the viscous flow properties which are characterized by the penetration value and the susceptibility become important since they govern the ability of the pavement to resist deformation under stress. Unfortunately, most bitumens are too hard and brittle at low temperatures and too soft and deformable at elevated temperatures so that great care must be exercised to minimize low-temperature cracking without incurring excessive distortion at elevated temperatures.

An examination of the literature reveals a bewildering number of attempts by practitioners to overcome this frustrating limitation through the control of susceptibility or the use of additives such as reinforcing fabrics,⁵ plastic grids,⁶ reclaim rubber,⁷⁻⁹ fibrous fillers,^{10,11} or sulfur,⁴ some of which have found limited application where the additional cost justifies their use. Recently, attention has been directed to the use of polyethylene as a bitumen modifier following the successful development of a patented paving mix under the Novophalt tradename in Austria.¹²⁻¹⁴

Polyethylene is attractive as a bitumen modifier for several reasons, the most important of which is cost. The global production of polyethylene in 1984 exceeded 20 million tons, an amount which also generated huge quantities of reclaim and scrap polyethylene at prices not much different than that of the bitumen binder itself.¹⁵ Current efforts to recover polyethylene from municipal waste could provide an additional source of supply.

The polyethylenes are long-chain hydrocarbon molecules derived principally from the polymerization of ethylene. Such polymeric molecules may be modified by copolymerization with other monomers, or by the method of polymerization, to provide a large family of materials which are commonly characterized by their molecular weight, composition, density, melting point, and degree of branching. The simplest member of the family is linear polyethylene, a highly crystalline polymer with an isotropic melting transition near 133°C, which is the maximum melting temperature for non-oriented molded specimens. As the polyethylene molecule is modified through branching or copolymerization, the degree of crystallinity, the density, and the melting temperature correspondingly decrease. By such control of the polyethylene structure a very large number of commercial polyolefin grades has been created for the plastics industry. These polyethylenes, broadly speaking, are frequently designated according to density as in the case of high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). The low-density (0.90–0.94 g/cm³) polyethylenes commonly have melting transitions in the 100–115°C range.

The dispersion of polyethylene in bitumen is readily accomplished at elevated temperatures under high shear conditions. At temperatures above 140°C, the molten polyethylene particles will gradually absorb the aliphatic

maltene components of the bitumen and partially dissolve to form a highly viscous, elastic dispersion. Mark and Gragger¹⁶ have described the viscoelastic behavior of polyethylene-bitumen mixtures from a fundamental point of view to explain the influence of added polyethylene on the high- and low-temperature creep properties of Novophalt pavements. Since polyethylene is solid and crystalline below its melting transition, the dispersed polyethylene particles assume the characteristics of a filler at temperatures near 50°C when the bitumen matrix becomes soft and deformable. As a consequence, the Novophalt pavements possess increased resistance to deformation (such as rutting) at elevated temperatures (but below the melting transition of polyethylene). Additional benefits include greater tensile strength, increased impact fracture toughness, greater fatigue resistance, and a lowering of the brittle temperature, all of which contribute to an extended pavement service life. Paving trials in Austria, the United Kingdom, and Italy during the past ten years have confirmed the laboratory expectations, involving computer analysis, that the service life of a Novophalt pavement can be 2.7–2.9 times longer than that of a standard paving formulation without such modification.¹²

As might be expected, the increased viscosity requires additional energy to mix the polyethylene-modified bitumen with aggregate. This can be a serious disadvantage in the case of hot-mix asphalts where residence times in the pug mill are measured in seconds. Another disadvantage is the tendency of the polyethylene particles to float to the surface of the liquid bitumen where they coalesce into a highly viscous layer which cannot be easily redispersed. Such disadvantages have been partly resolved through the use of processing aids such as dispersing agents, viscosity depressants, wetting agents, and emulsion stabilizers. Thus Novophalt mixtures commonly contain a minor proportion of atactic (amorphous) polypropylene and fatty acid derivatives to facilitate the process and optimize the performance.^{12,16}

In this investigation the objective was to develop a polyethylene-modified bitumen which would confer resistance to low-temperature cracking in hot-mix asphalt paving materials. The low-temperature cracking of asphalt concrete samples may be determined by the critical temperature (T_c) method proposed by Fromm and Phang² in which T_c is defined as the temperature at which an asphalt concrete can no longer flow fast enough to relieve the stress (in a restrained rectangular specimen) as it attempts to contract because of decreasing temperature. This critical fracture stress approach has been applied by Sugawara, Kubo, and Moriyoshi³ using a beam flexure test. The temperature at which the peak flexural stress occurred was defined as the transition point (T_r) for samples of asphalt concrete as a function of temperature and rate of strain.

Since it is the nature of the binder that is largely responsible for low-temperature cracking⁴ small rectangular beams were cast from the bitumen-polyethylene dispersions and tested in flexure at low temperatures in order to observe any changes in ductility attributable to the polyethylene additive. This initial evaluation process was then used to select the more promising bitumen mixtures for further evaluation and testing in paving compositions according to ASTM D1559 Marshall methods.¹⁹

In addition to Marshall flow and stability tests on selected asphalt concretes, a few experiments measured the dynamic stiffness at two temperatures (5° and 23°C) according to the method of Emery.²⁰

MATERIALS

An 85/100 penetration-grade asphalt obtained from the Gulf refinery in Clarkson, Ontario, a residual bitumen from western Canada crude, was selected for the low-temperature flexural tests. For the mix design tests, an 85/100-grade asphalt from the British Petroleum (BP) refinery in Bronte, Ontario was chosen. The physical properties of these two bitumens are summarized in Table I.

Several types of polyethylenes were examined during the course of this investigation. The list in Table II excludes high-density polyethylene since difficulties were experienced in dispersing this type of polyethylene with the low-torque laboratory high-speed mixer. The low-temperature flexural tests employed commercial-grade Exxon Escorene LPX-1 (LLDPE) in one series and a scrap reclaim polyethylene (National Pro Industries) which contained carbon black, dicumyl peroxide (2 percent by weight), and various other unspecified additives in another. The remaining polyethylenes included a series obtained through the courtesy of D. H. Robinson of the Dupont Research Centre in Kingston, Ontario and a series of poly(ethylene-co-vinyl acetate) resins (CIL Evatanes) recommended for the modification of asphalt paving materials.²¹ It will be apparent that the polyethylenes listed in Table II have widely different molecular weights (as indicated by their melt flow index values ranging from 0.6 to 150 g/10 min). These polyethylene resins were used to study the interrelationship between the molecular weight or composition of the polyethylenes (including the vinyl acetate copolymers) and the resulting degree of dispersion, viscosity, and mixing characteristics. These independent experiments were needed to identify the influence of polyethylene structure and molecular weight on the ease of dispersion and the degree of subdivision of the polyethylene particles in the bitumen when subjected to high-speed stirring at elevated temperatures. The viscosities of the molten dispersions were also determined since the increased viscosities of the bitumen-polyethylene dispersions required

TABLE I
Properties of Asphalts Used in Study^a

	Gulf Clarkson		BP Bronte	
	Unaged	Aged ^b	Unaged	Aged ^b
Viscosity, Pa-s, 60°C	142.4	362.8	113.3	258.8
Penetration, 25°C	97	52	103	62
Ductility, 4°C	150+	—	107	—
25°C	150+	150+	150+	150+
Flash point (°C)	306	—	316	—
Relative density, 15.6°C	1.031	—	1.029	—

^a Tests were done by the Ontario Ministry of Transportation and Communications, Bituminous Research Department.

^b Thin film oven test.

TABLE II
Polyethylene Properties

	Melt index (g/10 min)	Density (g/cm ³)	Molecular weight distribution
Exxon Chemicals (Escorene LPX-1)	1.0	0.918	—
Dupont 11D-1	0.6	0.919	narrow
Dupont 11H	1.2	0.919	narrow
Dupont 19D	4.6	0.960	medium
Dupont 2107	5.1	0.924	narrow
Dupont 2111	20	0.924	narrow
CIL (Evatane 18-150)	150	0.93	broad
CIL (Evatane 28-150)	150	0.94	broad
CIL (Evatane 33-25)	25	0.95	broad
National Pro Industries (scrap reclaim)	2.0	0.93	broad

longer mixing times with aggregates in commercial-size pug mills, an important factor with respect to cost considerations. In a few experiments, an attempt was made to stabilize the polyethylene dispersions by adding a small proportion of a block or graft copolymer such as Shell Chemical Kraton G-1652.²² The properties of this ABA-type block copolymer have been reproduced in Table III.

Preparation of Flexural Test Bars

Weighed quantities of powdered polyethylene were dispersed in 400 g of bitumen heated to 150°C using a Silverson (Model L2R) high-speed mixer with a standard shearing ring. The heated fluid mixtures were then poured into an aluminum rectangular window-type mold (3.2 mm thick) clamped to a glass base plate. After filling the mold cavity with the molten bitumen dispersion, a second glass plate was placed onto the surface such that a smooth rectangular test bar (80 × 25 × 3.2 mm) was formed. The mold surfaces were lightly coated with a silicone grease to avoid adhesion of the bitumen sample to the mold. The assembly was fastened together with large

TABLE III
Properties of Kraton G-1652 at 23.3°C

Property	
Tensile strength ^a , Pa	1.424 × 10 ⁸
300% Modulus, Pa	4.92 × 10 ⁵
Elongation, %	500
Hardness, Shore A	75
Specific gravity	0.91
Brookfield viscosity ^b , cP	550
Styrene/rubber ratio	29/71
Physical form	Crumb

^a ASTM method D412 tensile test (rate of extension 254 mm/min).

^b Toluene solution containing 25% Kraton G at 25°C.

Source: Shell Chemical Co., Technical Bulletin Sc:65-75, "Kraton G Thermoplastic Rubber for Sealants, Adhesives and Related Materials."

alligator clips and placed in an ice bath to chill and solidify the samples before removing them from the mold. Each specimen was carefully removed and stored in a refrigerator at -20°C until required for flexural testing.

Viscosity Measurements and Microscopy

The viscosities of the liquid dispersions were measured at several temperatures and concentrations using a Brookfield viscometer with an RV spindle number 2. Small drops of the mixtures were removed at intervals and placed onto a heated microscope slide. By immediately placing a second heated slide on top of the droplet and squeezing the two glass slides together a thin film of the dispersion was formed which could be viewed by transmitted light under a microscope. Particular attention was directed at the limiting size of the dispersed polyethylene particles after prolonged high-speed stirring.

Low-Temperature Flexural Testing

The rectangular test specimens were removed from the storage freezer and placed in a specially constructed environmental chamber constructed from plywood and polystyrene foam insulation and attached to an Instron Tester. The design of the testing chamber is illustrated in the photograph and schematic drawing in Figures 1 and 2. A 3-point bending jig was mounted inside the environmental chamber to accommodate the rectangular test specimen. The twin supports and loading nose had 6.35 mm radii and a 50 mm fixed span. By trial and error, the crosshead speed was eventually set at 1.27 mm/min for all tests. Each test specimen was preconditioned for

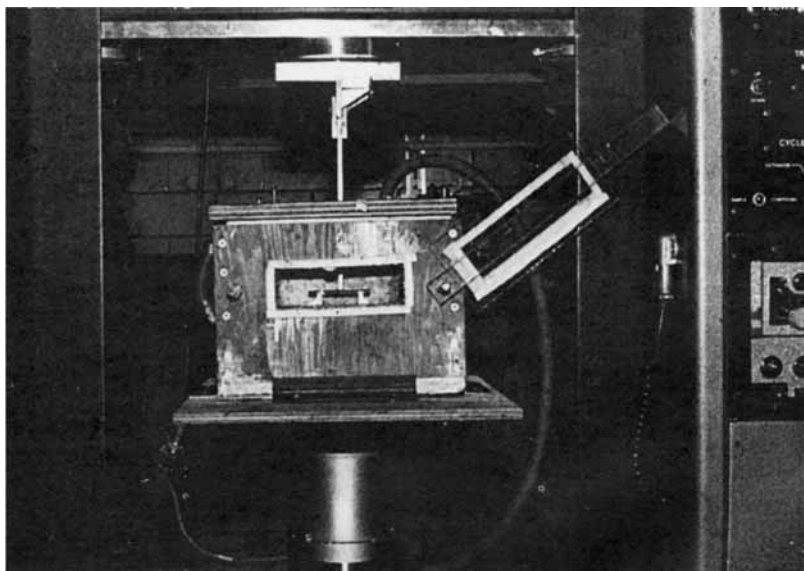


Fig. 1. The 3-point flexural jig was mounted inside an insulated wooden box attached to an Instron Tester. The temperature of the rectangular test specimen was regulated by compressed air chilled with liquid nitrogen.

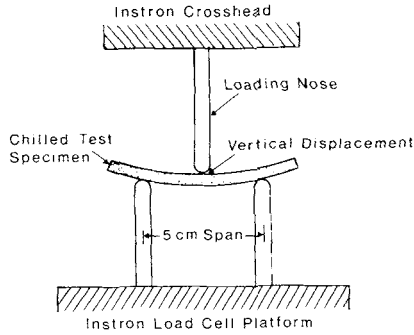


Fig. 2. A plan view of the testing apparatus illustrates the three-point bending mode of the test specimen. The span to depth ratio was approximately 16.

30 minutes at the test temperature in the environmental chamber before initiating the test. The temperature was controlled by passing compressed air chilled by liquid nitrogen through the chamber.

Paving Formulation

Two different aggregates designated "Medonte Disher Farrand" and "Durham" were selected for the mix design experiments. The particle size distribution of the Disher-Farrand (Medonte District) aggregate is reproduced in Figure 3. The trials were conducted in the Paving Research Laboratories of the Ontario Ministry of Transportation and Communications in Downsview, Ontario. In one series, BP Bronte 85/100 pen. bitumen was mixed with aggregate according to standard ASTM D1559¹⁹ procedures and compacted into Marshall briquets. Additional data was obtained with Gulf Clarkson 85/100 pen. bitumen but has been excluded since the results were similar. Marshall briquets were prepared at three bitumen concentrations (5.0, 5.5, and 6.0%) relative to the total weight of aggregate plus additional LLDPE (8% Escorene LPX-1 relative to the bitumen weight) and Kraton G (5% relative to the weight of bitumen) using the procedures outlined in the Asphalt Institute Manual.²³ Each briquet was tested for Marshall stability, Marshall flow, voids in the mineral aggregate (VMA), and air voids

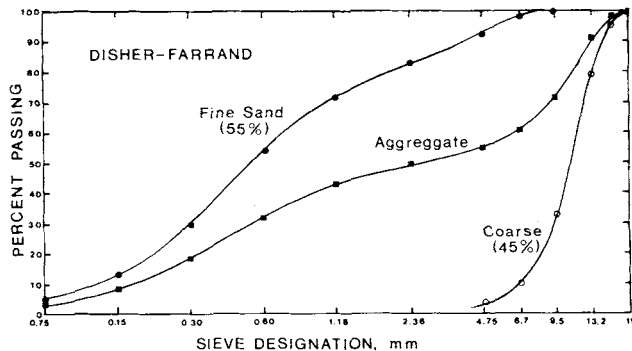


Fig. 3. The Disher-Farrand aggregate comprises 55% sand and 45% coarse crushed limestone in accordance with the MTC specification for HL-4 hot mix.

according to ASTM D1559. The Marshall water immersion test was completed for one specimen and compared with a standard HL4 mix. The resilient modulus (M_R) was measured at two temperatures (5° and 23°C) on several Marshall briquets using a dynamic loading duration of 0.1 second at a frequency of 20 cpm according to the published procedure of Emery.²⁰

RESULTS

The Brookfield viscosity values followed a similar pattern for each concentration over the temperature range from 120°C to 170°C as recorded in Figure 4 for LLDPE (Dupont Sclair 2107) dispersed in the Gulf Clarkson bitumen. No explanation was evident for the relatively small increase in viscosity when the LLDPE concentration was increased from 5% to 8%. However the Silverson high-speed mixer operated with increasing difficulty as the polyethylene concentration approached 10% so that the observed viscosity may also reflect differences in the degree of dispersion. While the solubility of the polyethylene in bitumen at these temperatures is unknown, it was apparent from the rubberlike quality of the mixture and the Weissenberg effect that at least partial solubility had occurred after prolonged heating and stirring. The viscosities recorded in Table IV were relatively insensitive to the molecular weight and composition of the polyethylene under these conditions which tended to indicate a rather low solubility of the polyethylene at these temperatures after 30 minutes of high-shear mixing. Dupont polyethylene sample 11 H is an exception which may reflect the difficulty in reproducibly measuring the viscosities of these unstable mixtures (due to gradual separation on standing).

When the logarithm of the viscosity was plotted versus the reciprocal of the absolute temperature, a linear Arrhenius relationship was found over the temperature interval from 100 to 160°C (Fig. 5). Note that at a concentration of 5% LLDPE the viscosity of the bitumen increased approximately tenfold, producing a consistency which would be difficult to mix with aggregates using commercial production equipment.

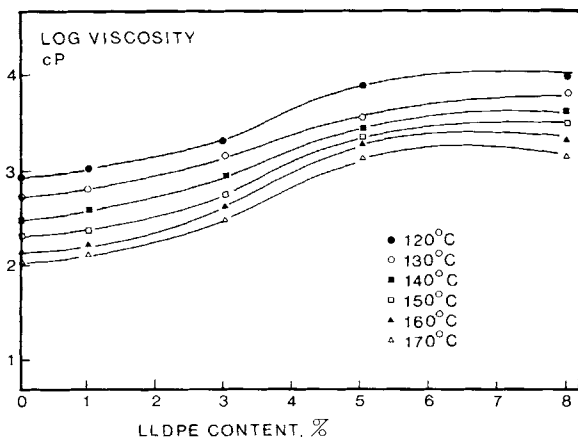


Fig. 4. The Brookfield viscosity values appeared to approach a limiting viscosity at 8 percent LLDPE concentration by weight in 85/100 pen. bitumen.

TABLE IV
Viscosities of Polyethylene-Bitumen Mixtures

Polyethylene type	Melt flow index (g/10 min)	Brookfield viscosity, cP	
		3% LLDPE at 150°C	5% LLDPE at 140°C
Dupont 11D-1	0.6	600	2840
Dupont 11H	1.2	762	7930
Dupont 190D	4.6	405	1320
Dupont 2107	5.1	430	1080
Dupont 2111	20.0	399	1010
CIL Evatane 18-150	150	263	880
CIL Evatane 28-150	150	242	920
CIL Evatane 33-25	25	293	820

Low-Temperature Flexural Testing

The force-displacement response for three cast specimens are reproduced in Figure 6 including the unmodified bitumen as reference (Gulf Clarkson 85/100 pen.). These typical responses clearly illustrate the dramatic influence of added polyethylene (Escorene LPX-1) on the mechanical properties—modulus, ultimate strength, ductility, deformation at fracture, and energy to fracture. As previously indicated, these samples are sensitive to the speed of testing so that slower strain rates often produced ductile deformations without fracture whereas faster rates caused abrupt fracture. For ease of comparison the crosshead speed was arbitrarily fixed at 1.27 mm/min in order to ensure brittle fracture in the majority of specimens at low temperatures (indicated by dashed lines in Fig. 6).

The addition of a minor proportion of Kraton G block copolymer seemed to further increase the energy to fracture as measured by the contained

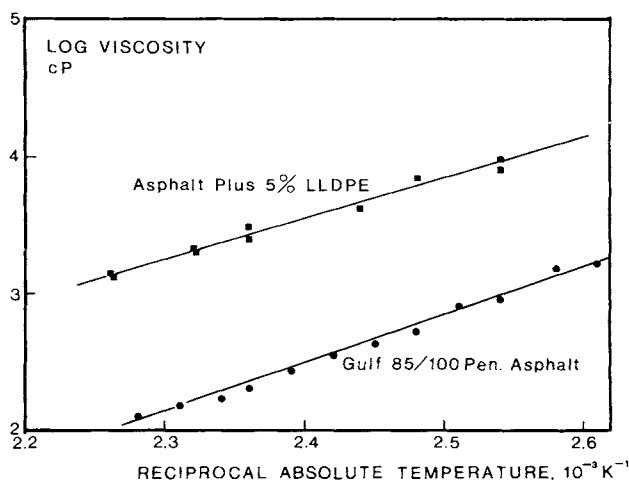


Fig. 5. When plotted on a logarithmic scale the viscosity of the 5 percent LLDPE bitumen suspension followed a linear Arrhenius relationship which was approximately ten times greater than that of the unmodified bitumen at the same temperature.

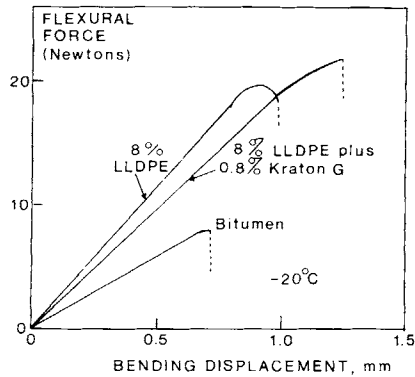


Fig. 6. The reproduced flexural force-displacement tracings from the Instron Tester illustrate the influence of LLDPE and Kraton G on the mechanical properties of bitumen at -20°C .

area under the force-displacement curve although the modulus (as indicated by the slope) was slightly reduced.

The addition of polyethylene gradually increased the flexural strength of the bitumen mixture and became quite marked at concentrations near 10% at temperatures of -30°C . However, the increase in strength was not appreciable until the polyethylene concentration exceeded 5% by weight (see Fig. 7).

The flexural modulus was quite sensitive to the temperature in the region from -10°C to -40°C as shown in Figure 8. The addition of 5% polyethylene (Escorene LPX-1) increased the flexural modulus in this temperature range but, unexpectedly, when the polyethylene concentration was increased to 10% by weight, the resulting modulus values were not too different from that of the unmodified bitumen control (except for one value at -40°C). Despite these differences, the stiffnesses of these mixtures at temperatures below zero Celsius are so large relative to those at 40°C , that creep distortion will be negligible for most traffic conditions.

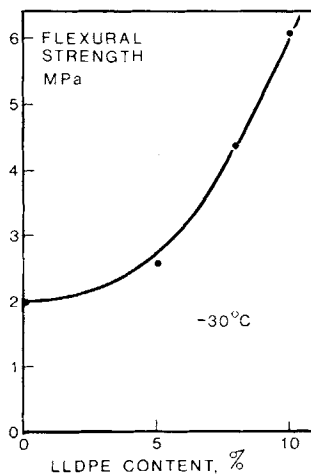


Fig. 7. The addition of polyethylene increases the flexural strength of the bitumen at -30°C although the increase is relatively small at polyethylene concentrations less than 5 percent by weight.

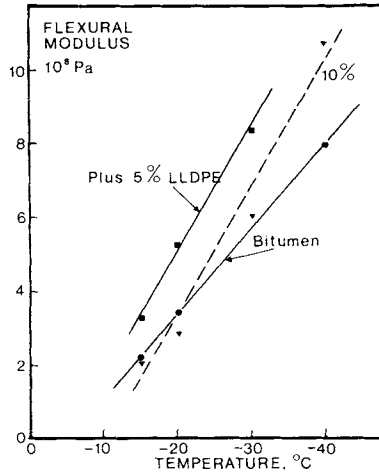


Fig. 8. The flexural modulus was sensitive to the temperature from -10° to -40°C . At 10 percent polyethylene the modulus is almost indistinguishable from that of unmodified bitumen except at -40°C .

Influence of Kraton G Block Copolymer on Mechanical Properties

Having established that the optimum concentration of polyethylene is between 5% and 10% by weight, attention was directed at the preferred concentration of the Kraton G block copolymer. The low-temperature flexural displacement at fracture appeared to reach a maximum near 0.8% by weight (relative to the bitumen) in most of the experiments as indicated in Figure 9 at a temperature of -20°C . However, the total energy to fracture as calculated from the area under the complete force-displacement curve presented a different picture as shown in Figure 10 at the same temperature (-20°C). Therefore, the maximum strain (or displacement) at fracture is not simply related to the toughness or energy to fracture. Note however, that the greatest response appears when the concentration of the polyethylene is 10% by weight and the Kraton G is near 1.5%. Unfortunately, at these

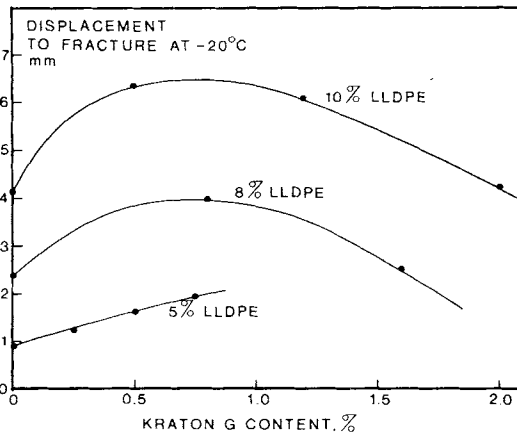


Fig. 9. The maximum displacement at fracture occurred when the Kraton G block copolymer content was near 0.8 percent by weight bitumen.

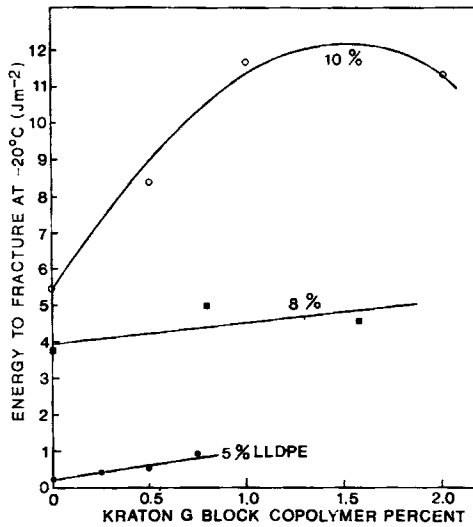


Fig. 10. The total area under the force-displacement diagram was more sensitive to the Kraton G content at 10 percent polyethylene and less significant at lesser polyethylene concentrations.

concentrations the viscosity of the bitumen mixture is so large that mixing with a mineral aggregate becomes much more difficult. In practice, the polyethylene concentration will be limited by the maximum binder viscosity that can be readily handled in commercial paving procedures.

When the energy to fracture was plotted in Figure 11 versus the polyethylene concentration at four different temperatures, it was apparent that

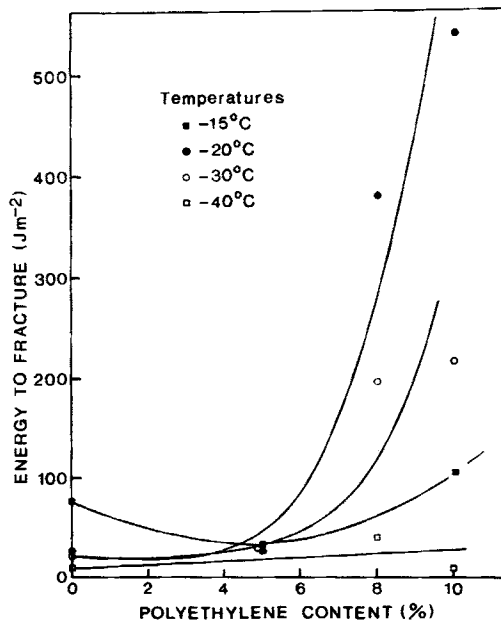


Fig. 11. The increase in fracture energy is most pronounced at polyethylene concentrations greater than 5 percent.

all the samples exhibited brittle fracture at -40°C at this strain rate. Moreover, the influence of polyethylene on the fracture toughness was less noticeable at concentrations below 5%. These results emphasize the necessity of incorporating more than 5% polyethylene if the desired ductility and fracture toughness are to be realized. Although the experimental error is obviously quite large, the same trend is evident at each temperature in Figure 11 until the temperature reached -40°C , at which temperature all the specimens failed in a brittle mode.

Low-Temperature Flexural Testing of Bitumen Containing Scrap Polyethylene

For economic reasons, it was important to determine if inexpensive scrap polyethylenes could be substituted for virgin polyethylenes. A previous survey by Svazic¹⁵ had revealed the availability of abundant supplies of scrap polyethylenes at prices well below the selling prices of comparable virgin polyethylenes. A 10-kg sample of scrap polyethylene was subsequently obtained from National Pro Industries Inc., Boucherville, Quebec, for comparison with the previously tested commercial polyethylene grades. The available information from National Pro Industries indicated that the scrap black wire coating compound had a melt flow index of 0.93 g/cm^3 and contained 2.0% dicumyl peroxide cross-linking agent. Weighed quantities of the pelletized scrap polyethylene were dispersed in 85/100 pen. Gulf Clarkson bitumen and cast into rectangular test bars as previously described. The flexural properties of these test bars are summarized in Table V and compared with the previously tested Escorene LLDPE control (with and without added Kraton G block copolymer). There are significant differences between the virgin and scrap polyethylenes which may be partially, at least, attributable to the presence of dicumyl peroxide, a reactive cross-linking and grafting agent. Both the fracture energy and the displacement to fracture are noticeably greater for the virgin LLDPE at the 8% concentration, particularly in the presence of added Kraton G block copolymer. Nevertheless, the displacement to fracture is consistently larger whenever polyethylene is present relative to the unmodified bitumen control. The advantages at the 5% polyethylene concentrations for both the virgin and scrap polyethylenes are not so evident however.

Bituminous Mix Design

The Marshall test results are summarized in Figure 12 for one series containing BP Bronte 85/100 bitumen as described in the experimental section. From these results the design mix in Table VI was considered near optimum for this series although further improvements are undoubtedly possible with refinement. These results reveal that the addition of polyethylene generally increases both the Marshall stability and Marshall flow at the same time. Only minor differences are apparent in the VMA values and the contained air voids after compaction compared with the HL4 control mix. Despite the greatly increased viscosity of the polyethylene-modified bitumen the hot mix appeared to mix and compact without difficulty, perhaps due to the extraordinary plasticity of the heated mixture which is

TABLE V
Mechanical Properties of Bitumen Containing Scrap Polyethylene^a at -20°C

	Composition		Properties		
	Polyethylene content (% by weight)	Kraton G content (% by weight)	Scrap polyethylene ^a	LLDPE control (Escorene LPX-1)	Bitumen control ^b
Flexural modulus (MPa)	0	0	—	—	3
	5	0	2.6	5.2	—
	5	0.5	3.5	2.5	—
	8	0	3.2	2.2	—
	8	0.8	3.2	2.9	—
Flexural strength (MPa)	0	0	—	—	2
	5	0	2.1	2.8	—
	5	0.5	2.3	2.1	—
	8	0	3.4	2.3	—
	8	0.8	3.5	5.2	—
Fracture energy (J/m ²)	0	0	—	—	26
	5	0	26.3	26.8	—
	5	0.5	22.2	35.1	—
	8	0	60.8	383	—
	8	0.8	54.0	490	—
Displacement to fracture (mm)	0	0	—	—	—
	5	0	2.6	2.0	—
	5	0.5	2.0	3.2	—
	8	0	3.2	5.0	—
	8	0.8	2.8	8.1	—

^a Gulf Clarkson Bitumen (85/100 pen.)

^b Exxon Ensorene LPX-1.

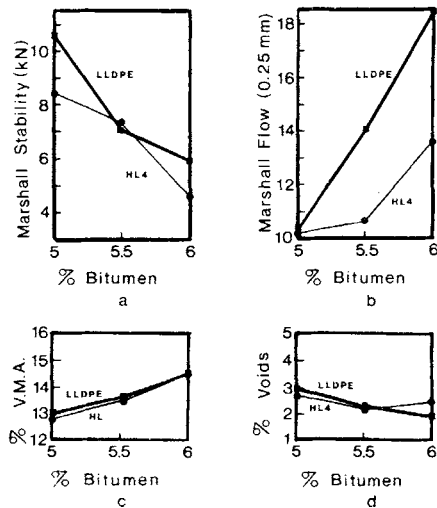


Fig. 12. The properties of Marshall briquets containing 8 percent LLDPE and 0.8 percent Kraton G are compared with a DHO HL4 hot mix paving standard for three bitumen concentrations.

TABLE VI
Bituminous Mix Design

	Parts by weight	
	Control mix HL-4	Modified
Coarse aggregate (Medonte Disher Farrand)	51	51
Fine aggregate (sand)	49	49
Bitumen (Bronte British Petroleum 85/100 pen.)	5.3	5.3
Polyethylene (Exxon LPX-1)	—	5.3
Block copolymer (Shell Kraton G)	—	0.42
Marshall flow (0.25 mm)	9.8	11.2
Marshall stability (N)	10,800	13,400
Air voids (% by volume)	4.6	5.4
Marshall water immersion test		
Retained marshall stability (%)	61.7	67.3

evident from the increased Marshall flow values (Fig. 12b). The 8% concentration of LLDPE (relative to the bitumen) was judged to be near the maximum concentration that could be readily mixed with aggregate in a commercial pug mill.

Resilient Modulus

Values of the resilient modulus for two experimental mixes have been plotted in Figure 13 and compared with the published data of Emery²⁰ for a typical paving mix which was designed for the Ontario region. For con-

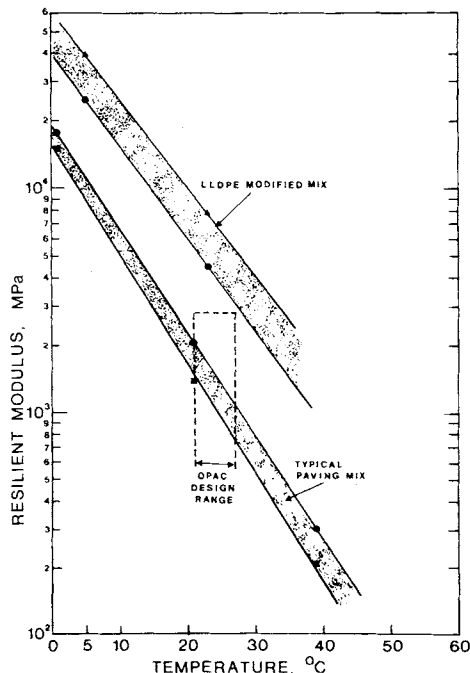


Fig. 13. The resilient modulus of the LLDPE - modified asphalt concrete at temperatures above zero degrees celcius is larger than that of a typical paving mix (paving mix data replotted from reference 20 for comparison).

ventional unmodified bitumen concretes the preferred resilient modulus values lie within the dashed region according to published guidelines in the Ontario Pavement Analysis of Costs (OPAC) report.^{29,30} These frequency measurements clearly illustrate the lateral displacement of the dynamic stiffness over the ambient temperature range. This increased stiffness at a particular temperature will also reduce the creep compliance which can be estimated from Nutting's empirical formula.³¹ The increased modulus at this frequency is also characteristic of Novophalt paving mixtures and clearly illustrates one of the principle advantages of polyethylene modification. The greater dynamic modulus reduces deformation, creep, and distortion of the pavement due to traffic, especially during warm weather. In this example the addition of 8% LLDPE to the bitumen has increased the stiffness so much that the temperature would need to be increased by 10 to 20°C to equal the dynamic stiffness of a conventional paving mix. In addition, the fracture toughness of this binder at -20°C as recorded in Table V has also been increased substantially (from 26 to 490 J/m²) so that the performance of this binder has been extended at both temperature extremes, a goal which has been the subject of many investigations during the past 50 years.

DISCUSSION

The low-temperature flexural properties of bitumen modified with polyethylene reveal that at low strain rates (corresponding to 1.27 mm/min crosshead speed) the maximum displacement at fracture, the flexural strength, the flexural modulus, and the energy to fracture are all simultaneously increased. Dynamic mechanical testing at traffic frequencies also confirmed the increase in resilient modulus of these paving mixtures over the full temperature range as previously observed by Denning and Carswell¹⁷ for Novophalt concrete. From these observations it would appear likely that the incidence of low-temperature cracking in polyethylene-modified paving concretes due to thermal shrinkage should be reduced at temperatures above -40°C since the modified binder is able to relieve stresses without fracturing by shear deformation.¹⁸ The critical temperature test proposed by Fromm and Phang² or the transition point method of Sugawara, Kubo, and Moriyoshi³ would provide more direct evidence concerning the validity of this conclusion using asphalt concrete test specimens instead of just the bitumen binder without mineral aggregate. Field tests initiated in 1977 in Austria confirm the laboratory expectations in terms of reduced rutting and "practically no cracking." This was particularly evident on the Prater Flyover bridge over the Danube river in Vienna which has been subjected to exceptionally heavy traffic and severe vibration.²⁴

It has been suggested by Gragger and Mark¹⁶ that the effectiveness of polyethylene in bitumen can be compared to the effect of rubber particles on the toughness and ductility of polystyrene (i.e., the well known ABS technology), where the rubber particles lower the threshold for crazing and prevent catastrophic cracking.¹⁸ This technique of increasing fracture toughness has been successfully applied to many other brittle plastics including bitumen.^{8,25,26,27} It is noted, however, that the effectiveness of the

disperse phase (in this example polyethylene) is dependent upon several factors including the particle size, the cohesion at the interface with the matrix, the glass transition temperature, and the relative softness (deformability) compared to the matrix. These factors should be kept in mind when attempting to disperse polyethylene in bitumen since the shearing conditions, dispersing agents, and molecular structure of the polyethylene component will influence the minimum attainable particle size and the cohesion between the phases. Since the desired ductile shear flow is greatest for small particles in the 0.1 to 10 μm diameter range, the mixing conditions must be carefully controlled to permit such a high degree of subdivision. Although high-speed stirring with a shearing ring was used in this study, other methods of mixing (such as in an extruder) can be usefully employed for this purpose. It is also advantageous to employ dispersing agents (such as compatibilizing block copolymers) to facilitate the dispersion, provide a cohesive interface, and to stabilize the hot liquid suspension so that separation does not occur after standing for long periods without agitation. In the patented Novophalt process, amorphous (atactic) polypropylene has been employed for this purpose but not very effectively. Experience has demonstrated that the dispersing aid should be of the AB block copolymer type with a large molecular weight in which one segment of the block copolymer is compatible with the disperse phase and the other segment is compatible with the matrix phase.²⁸ Under such ideal conditions very large increases in toughness and pseudoductility can be realized. Provided that relatively inexpensive scrap polyethylene can be employed for such modification and the amount of dispersing agent can be kept to a minimum, the total cost of producing such mixtures should not be excessive. These results indicate that the quality or type of polyethylene employed as an additive may be less important than the degree of dispersion and the interfacial cohesiveness. If this is indeed correct, then less consideration need be attached to the quality and composition of the available scrap polyethylenes, an important consideration in view of the diverse nature of the available scrap materials in terms of composition, molecular weight, and crystallinity. However, it is necessary that the polyethylene raw material scrap not be crosslinked or it will not adequately disperse.

A photograph of a typical dispersion containing 10% polyethylene is reproduced in Figure 14. Note the black asphaltene particles interspersed between the lighter (polyethylene) regions. Under ideal conditions the polyethylene phase consists of irregular shaped domains of approximately 10 μm . These lower density domains will coalesce at elevated temperatures in liquid bitumen and rise to the surface to form a coherent mass which can be difficult to redisperse. For this reason it is desirable to incorporate a dispersing agent or stabilizer to prevent or at least retard such coalescence.

The increased viscosity of the modified bitumen requires additional mixing time or increased mixing temperatures in the pug mill. The viscosity may be reduced by selecting a less viscous bitumen as the starting material instead of the 85/100 pen. grade chosen for this study. Still to be resolved is the preferred bitumen viscosity for a particular geographical region.

Denning and Carswell¹⁷ stress the need for special attention during rolling and compaction of the aggregate mix since the Marshall stability and

density can be greatly altered by the conditions of rolling. Below 120°C the mix becomes increasingly difficult to compact as the polyethylene begins to crystallize.

As indicated in Table VI, polyethylene modification increases the wet strength of the Marshall briquet (i.e., reduced water sensitivity). Although the difference is slight (5.6%) the control briquet decreased from 21.8 kN to 13.4 kN while the corresponding polyethylene-modified specimen decreased from 32.0 kN to 21.5 kN. Thus, the retained strength of the latter was equal to that of the dry control, which is particularly significant. Other studies report increased resistance to organic solvents, greater oxidation resistance, and greater fatigue resistance of pavements containing polyethylene.^{12,16,24} Skid resistance of polyethylene-modified asphalt concrete paving surfaces is unchanged.¹⁷ As in the case of elastomers, polyethylenes possess very low glass transition temperatures, often less than -80°C, a characteristic which may be necessary for increasing the low-temperature fracture toughness and ductility of bitumens.⁸ Other thermoplastics having glass transition temperatures greater than polyethylene would be less efficient. It should be noted that linear polyethylene possess one of the lowest glass transition temperatures (near -120°C) of all polymeric materials, including elastomers.

CONCLUSIONS

It has been demonstrated that most grades of polyethylene can be readily dispersed in heated liquid bitumen by high-shear mixing at temperatures near 140°C to form a colloidal suspension. The stability and performance of the resulting dispersion can be influenced by the conditions of mixing and the presence of dispersing agents such as block copolymers. The addition

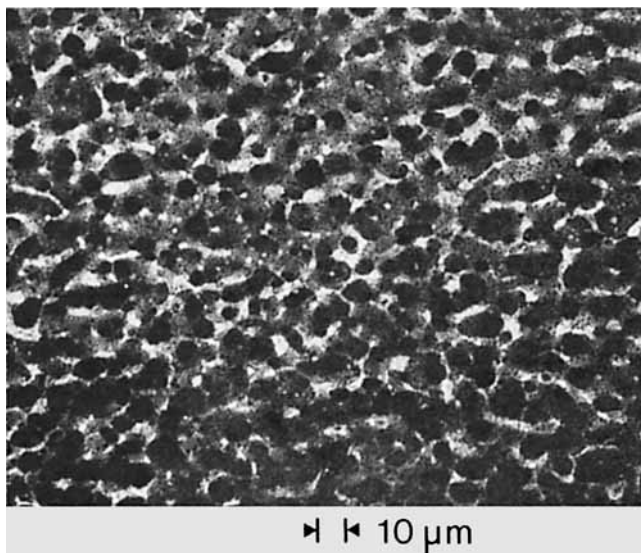


Fig. 14. In a typical dispersion the polyethylene phase can be distinguished as irregular shaped light colored regions interspersed between black asphaltene particles about 10 microns in diameter.

of even a few percent of polyethylene to bitumen can produce a large increase in the viscosity of the mixture so that special care must be exercised when mixing the modified bitumen with aggregate and applying the resulting hot mixture to road surfaces.

Flexural testing of the polyethylene-modified binder revealed that the mechanical properties were sensitive to the concentration of polyethylene over the region from 0 to 10% by weight. In general, the addition of polyethylene (LLDPE) increased the flexural (and tensile) strengths, the flexural modulus, the ultimate elongation, and the energy to fracture. The presence of Kraton G block copolymer further contributed to the strength, elongation, and toughness, but slightly reduced the modulus. From these findings, an attempt was made to design an optimum hot-mix paving formulation using a typical aggregate. Marshall briquets were prepared and compared with a standard HL4 mix used extensively by the Ontario Ministry of Transportation and Communications (MTC). Dynamic testing of the briquets confirmed that the presence of polyethylene produced a marked increase in the resilient modulus in the 0–40°C temperature range. These findings are consistent with the previously published data on the patented Novophalt system. Furthermore, the observed flexural properties of the modified binders at low temperatures indicated that the addition of polyethylene aided ductility and should therefore be beneficial for reducing the incidence of low-temperature cracking in asphaltic pavements. Although paving practices in Europe do differ from those in North America, it seems apparent that with proper formulation, the addition of polyethylene can more than double the life expectancy of a conventional hot-mix paving system without a substantial increase in cost, particularly if scrap polyethylenes can be utilized as raw material.

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