PERFORMANCE RANKING OF POYPHOSPHORIC ACID, REACTIVE ELASTOMERIC TERPOLYMER, AND STYRENE BUTADIENE MODIFIED BITUMENS IN DUCTILE FAILURE

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ABSTRACT

With the implementation of the Superpave™ bitumen specification by most North American user agencies, it has frequently become necessary to employ modifiers and/or special processing technology. While the specifications embodied in the AASHTO M320 standard were intended to be performance-based and hence blind to bitumen source and modification method, in reality many user agencies are still compelled to specify only certain types of modifiers and ban others. This situation has led to a continued search for improved specification tests with results that can better predict the performance in service. This paper discusses various ductile failure (fatigue) performance aspects of widely used Polyphosphoric Acid (PPA), Reactive Elastomeric Terpolymer (RET), and Styrene Butadiene (SB) modified bitumens. The experimental findings show that RET and SB have similar performance advantages over unmodified and PPA-modified materials. Ongoing pavement trials at various locations in Ontario, Canada, are briefly reviewed to shed further light on the relative benefits of the modifiers investigated. It is expected that the implementation of enhanced specification tests will allow user agencies to better pay for performance without the use of arbitrary specifications and/or bans on certain modifiers.

Keywords: modified bitumen, specification grading, polyphosphoric acid, reactive elastomeric terpolymer, styrene butadiene

1. INTRODUCTION

1.1 Superpave specifications

The introduction of the Superpave specifications in much of North America has led to a glut of low-cost bitumen modifiers and modification technologies (for instance, see [1-18] and others). Many of the materials produced are designed to reach the highest possible grade span (i.e., difference between low and high temperature Superpave grades, XX-YY) at a low cost. Nearly all of these approaches either increase the asphaltene fraction [2, 5, 6, 8, 13, 16], or make the available asphaltenes less soluble in the oily phase [7, 9, 10, 14, 17, 18], or utilize some type of chemical additive to produce a gel-type bitumen [1, 3, 4, 12]. Materials formed can be characterized by their non-Newtonian behaviour, delayed elasticity, high Penetration Index (PI), or reduced strain tolerance as reflected by a diminishing ductility and Critical Crack Tip Opening Displacement (CTOD) [19-23]. While some researchers have argued that a modest amount of gel formation is desirable [24], it is generally recognized that such materials are prone to oxidative and reversible hardening and that they often crack prematurely [19-21, 25-29]. Figure 1 shows an example of how quality bitumen compares to that modified with paraffinic Waste Engine Oil (WEO) residue with the aim of increasing the Superpave grade span [17].

FIGURE 1 – Performance variation for bitumens of nearly identical Superpave grades but different rheological type (sol-type versus gel-type). *Note:* These are representative photographs for adjacent paving contracts. The first was constructed in 2000 with polymer-modified bitumen whereas the second was constructed in 1998 with bitumen blended with WEO residue. The poor performer carries only about 60% of the average daily traffic compared to the good performer. The only explanation for this huge performance difference was found to be the difference in bitumen rheological type and thus quality [17].

Superpave was designed to limit fatigue cracking by specifying a limit on the bitumen's loss modulus (G"), which was considered to be directly and fundamentally linked to this distress. A limit of 5,000 kPa was imposed on the ambient temperature G" to control fatigue cracking. It was thought that bitumen with a high G" would dissipate more energy through fatigue. However, G" reflects the dissipation of energy through both viscous and damage processes thus confounding this argument. Furthermore, G" is typically measured in the linear viscoelastic regime at low strains while fatigue is a high strain phenomenon. Hence, it has proven difficult to correlate G" with fatigue in service and the limit on this property has largely been abandoned as an acceptance criterion [23].

The low temperature creep stiffness (S(t)) was initially limited by the Superpave specification to 200 MPa in order to control transverse cracking. However, those responsible for the implementation of this criterion considered 200 MPa to be too restrictive and raised it to 300 MPa. In a somewhat arbitrary fashion, a lower limit of 0.3 was imposed on the slope of the creep stiffness master curve (m(t) or m-value). The changes were meant to exclude the use of highly air blown materials, known to possess low m-values and considered prone to early cracking from thermal fatigue [30].

1.2 Ductile failure

A significant number of researchers have proposed alternate grading tests and specification criteria in response to the conflicting reports on the accuracy of the Superpave specifications. As it goes beyond the scope of this paper to review the entire literature, this discussion focuses on a brief review of our efforts in this area and, in particular, the development of the Double-Edge-Notched Tension (DENT) test protocol.

Fatigue cracking can simply be described as an opening up of free surfaces within the pavement structure due to imposed stresses and strains at ambient and low temperatures. Cracking occurs when a critical strain is exceeded prior to the stress state changing from one of pure tension to one of compression as the pavement flexes to a degree before confinement by the subgrade and surrounding asphalt becomes predominant. Cracks will not form if the strain tolerances of the bitumen, mastic, and asphalt exceed the available strain as limited by the confinement. Hence, we have proposed the use of an approximate CTOD for the specification grading of bitumens to control fatigue [23]. The CTOD represents the strain tolerance of a ductile material in the presence of a sharp notch and severe confinement. The DENT test was developed to measure an approximate CTOD in a simple manner analogous to the measurement of a ductility or force-ductility.

Using the CTOD as a specification criterion provides an improvement over use of the ductility and force-ductility properties, since it measures the strain tolerance of a small fibre (fibril) of bitumen, which is a better reflection of how the material fails in the asphalt. In regular ductility and force-ductility tests, a large fraction of the energy is dissipated as non-essential work in areas away from the actual failure zone. This type of failure contrasts with what happens in asphalt, where the process is highly localized between large aggregate particles.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Materials

The materials used in this study were obtained from various commercial sources. Two types of bitumens were used for the modification experiments. Cold Lake 80/100 penetration grade bitumen was obtained from the Imperial Oil of Canada refinery in Edmonton, Alberta. Cold Lake is a crude that produces good quality bitumen low in waxes (paraffin and/or microcrystalline) and hence suffers little from chemical or physical hardening. A second bitumen distilled from a blend of offshore crudes was obtained from the Shell Canada refinery in Montreal, Quebec. The suppliers for both materials had graded them under the Superpave specifications as PG 58-28.

The Polyphosphoric Acid (PPA) modifier was obtained from the Sigma-Aldrich Chemical Company as a 115% equivalent H_3PO_4 material and was used as purchased.

The Reactive Elastomeric Terpolymer (RET) modifiers were obtained from the E.I. du Pont Chemical Company. Two different grades of RET were used for this study: Elvaloy® RET AM and RET 4170.

The Styrene-Butadiene (SB and SBS) type modifiers were obtained from Kraton Polymers. Several different grades of both SB diblock and SBS triblock copolymers were used for this study: D1101 triblock, D1102 triblock, D1118 diblock, and D1192 triblock. The D1192 is a so-called high vinyl grade with a large proportion of vinyl functional groups in side chains. This proportion is supposed to increase the oxidation stability of the polymer in service. Sulfur was used at 0.1% by weight of the mixture to compatibilize the SB-type polymers with the base bitumen according to standard procedures.

A complete list of the bitumen compositions investigated in this project is provided in Table 1. The data show that all modifiers increase the high temperature grades by significant amounts and that the low temperature grades are affected by lesser amounts. The exceptions here are PG 58-28 + 1.2% PPA (sample N) and PG 58-28 + 1.5% RET AM + 0.3% PPA (sample Q), since the low temperature grades for these two bitumens appear to have deteriorated significantly compared to the unmodified PG 58-28 (sample M). Such deterioration suggests gelling of the material.

2.2 Experimental procedures

The modified bitumens were prepared according to standard procedures. PPA was slowly added to the hot bitumen, followed by an additional hour of mixing. RET was slowly added under high shear to the bitumen, followed by 15 minutes of mixing, after which PPA catalyst was added, followed by an additional hour of mixing. SBS modification was done by slowly adding the polymer under high shear, followed by 15 minutes of mixing, after which the sulfur was added, followed by an additional hour of mixing. Mixing temperatures were kept between 165°C and 170°C.

All straight and modified bitumens were graded according to Superpave protocols as embodied in the American Association of State Highway and Transportation Officials (AASHTO) standard M320 [31].

The essential and plastic works of failure and CTOD were determined according to the protocols described in Ministry of Transportation of Ontario Laboratory Standard 299 (LS-299) [32]. In brief, samples were conditioned at the test temperature for 24 hours. Double-edge-notched tension specimens of 10 mm thickness with ligaments (i.e., distance between the two opposing notches) of 5 mm, 10 mm, and 15 mm, were tested at 50 mm/min until failure. Figure 2 provides a photograph of three specimens in the ductility bath. Duplicates were obtained for each ligament, and the repeatability was generally found to be good to excellent.

The area under the force-displacement curve provided the total work of failure (W_t, J). The total work of failure divided by the ligament cross sectional area ($L \times B$, m^2) gave the specific total work of failure for each ligament length (w_t, J/m^2). The specific total work of failure was plotted versus the ligament length, and the intercept of this straight line provided the specific essential work of failure (w_e, J/m^2), while the slope provided the specific plastic work of failure term (βw_p, J/m^3) (see Figure 3(c)). The specific essential work of failure divided by the net section peak stress in the smallest ligament length (σ_n, N/m^2), provided an approximate CTOD (m). The CTOD is approximate because the net section peak stress in the smallest ligament length is used as a surrogate for the true yield stress, saving the time of having to measure the yield stress with a regular dog bone specimen [23].

Table 1 – Investigated Bitumen Compositions

Code	Base Bitumen	Modifier and Content	Catalyst	Superpave Grade (Span), °C
A	80/100	-	-	67-28 (95)
B	80/100	PPA, 1.2%	-	78-30 (108)
C	80/100	RET 4170, 1.3%	PPA, 0.3%	77-29 (106)
D	80/100	RET 4170, 1.3%	PPA, 0.6%	78-32 (110)*
E	80/100	RET 4170, 1.3%	-	74-29 (103)
F	80/100	RET AM, 1.8%	PPA, 0.3%	79-29 (108)
G	80/100	SBS D1101, 2.5%	-	75-27 (102)
H	80/100	SBS D1101, 2.5%	S, 0.1%	74-29 (103)
I	80/100	SBS D1102, 2.5%	S, 0.1%	72-30 (102)
J	80/100	SB D1118, 2.5%	S, 0.1%	73-29 (102)
K	80/100	SBS D1192, 2.5%	S, 0.1%	73-28 (101)
L	80/100	SBS D1192, 2.5%	S, 0.2%	73-30 (103)
M	58/28	-	-	62-31 (93)
N	58-28	PPA, 1.2%	-	78-24 (102)
O	58-28	RET 4170, 1.2%	PPA, 0.3%	76-32 (108)
P	58-28	RET 4170, 1.3%	PPA, 0.6%	75-32 (107)
Q	58-28	RET 4170, 1.5%	-	71-32 (103)
R	58-28	RET 4170, 1.5%	PPA, 0.3%	80-26 (106)

Note: PPA is Polyphosphoric Acid (modifier or catalyst), RET is Reactive Elastomeric Terpolymer, SB is Styrene-Butadiene, SBS is Styrene-Butadiene-Styrene, and S is Sulfur. * Cold Lake bitumen modified with 1.3% RET and 0.6% PPA gelled before the low temperature grade could be determined, so the temperature given is for the RTFO residue.

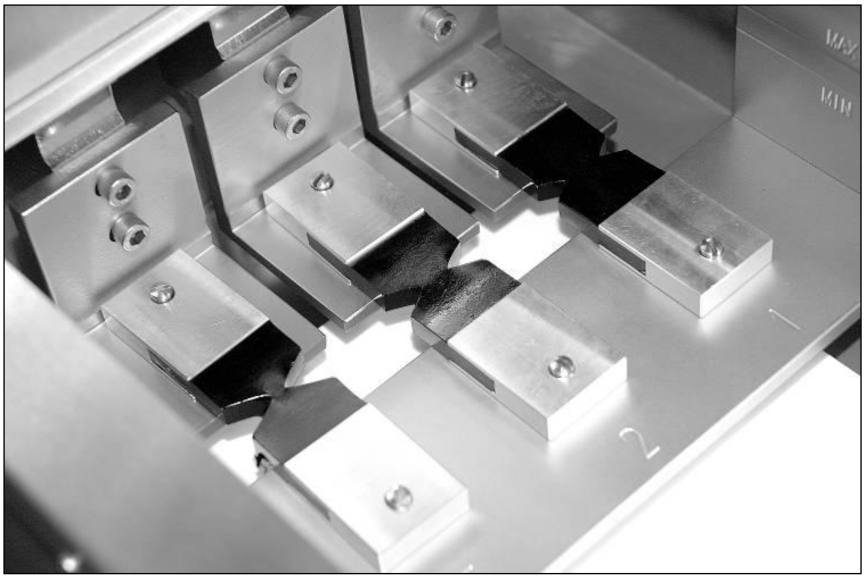
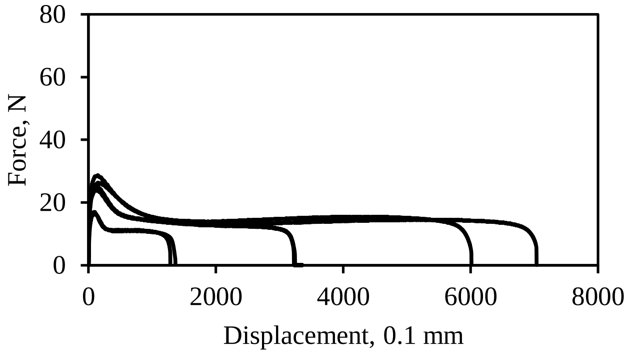


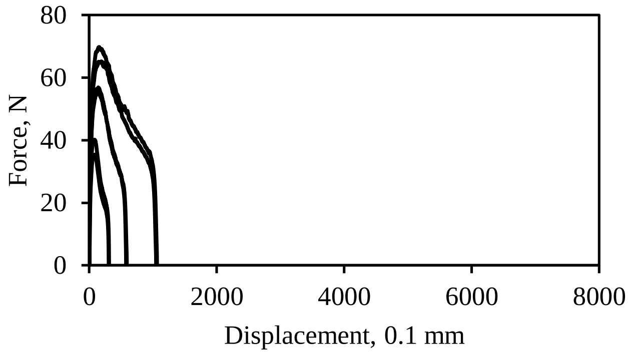
Figure 2 – Double-edge-notched tension (DENT) specimens just prior to conditioning and testing. *Note:* Ligament lengths shown are (1) 15 mm, (2) 10 mm, and (3) 5 mm.

3. RESULTS AND DISCUSSION

The results for duplicate DENT tests on SBS modified bitumen aged in RTFO and PAV are provided in Figures 3(a) and 3(b), respectively. The data analysis for both residues is provided in Figure 3(c). The specific essential works of failure (w_e), specific plastic work terms (βw_p), and CTODs for all compositions are compared in Figures 4-6.



(a)



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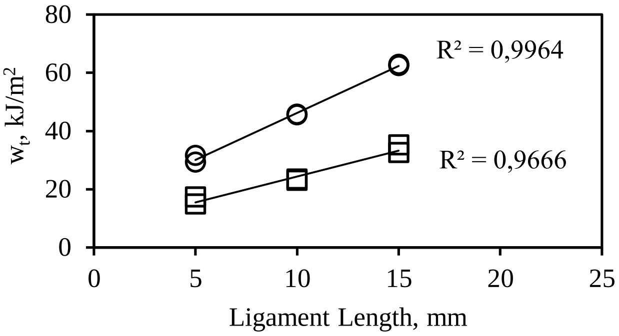

(c)

Figure 3 – Raw force-displacement data for replicate double-edge-notched tension tests on Cold Lake 80/100 + 2.5% SBS D1101 + 0.1% S after (a) RTFO and (b) PAV aging and (c) essential work of failure analysis for both bitumens. *Note:* The essential works of failure for the RTFO and PAV samples are 13.9 kJ/m^2 and 6.6 kJ/m^2, respectively. The CTODs for the RTFO and PAV samples are 41.5 mm and 8.7 mm, respectively.

The general repeatability of the DENT test is obviously very good. The findings from the essential work of failure analysis are interesting in several respects. First, the polymer modifiers all appear to increase the specific essential work, plastic work term, and CTOD by reasonable amounts. This contrasts to the findings for straight PPA modification, which appears to lower both the essential work and the CTOD (PAV residue in both base bitumens). Second, the changes in the failure properties for PAV residues in the SBS modified systems are significant. While these RTFO residues appear to be tougher than the RET systems, the advantage largely disappears after PAV aging. It is not clear if this early ductile failure advantage translates into any significant benefits in terms of pavement cracking performance as the PAV residue reflects the bitumen after only about three to four years of service [33-35]. Differences between base bitumens and oxidation states are more significant than differences between modifiers. However, straight PPA modified binders perform worst and possess the lowest CTODs, which could result in premature and excessive cracking in service. These findings are in agreement with an earlier study that found that

PPA consistently lowers the CTOD [13]. Combined with the findings of Table 1, where sample N lost 7°C from its low temperature grade due to PPA modification, caution is warranted.

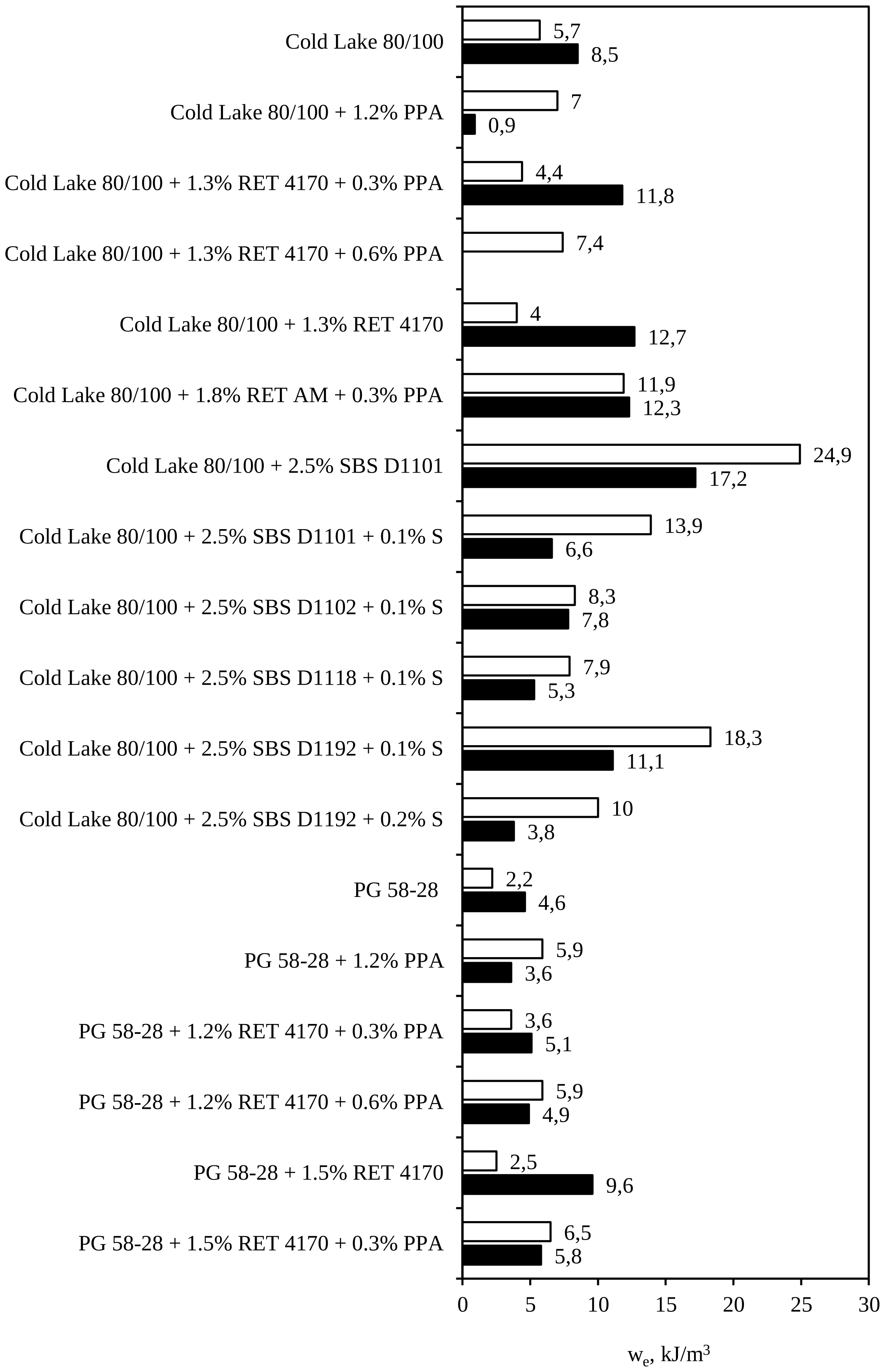

Figure 4 – Essential works of failure for all straight and modified bitumens. *Note:* Open bars are for RTFO residues and filled bars are for PAV residues. The PAV residue for Cold Lake bitumen modified with 1.3% RET and 0.6% PPA gelled during reheating and hence could not be tested.

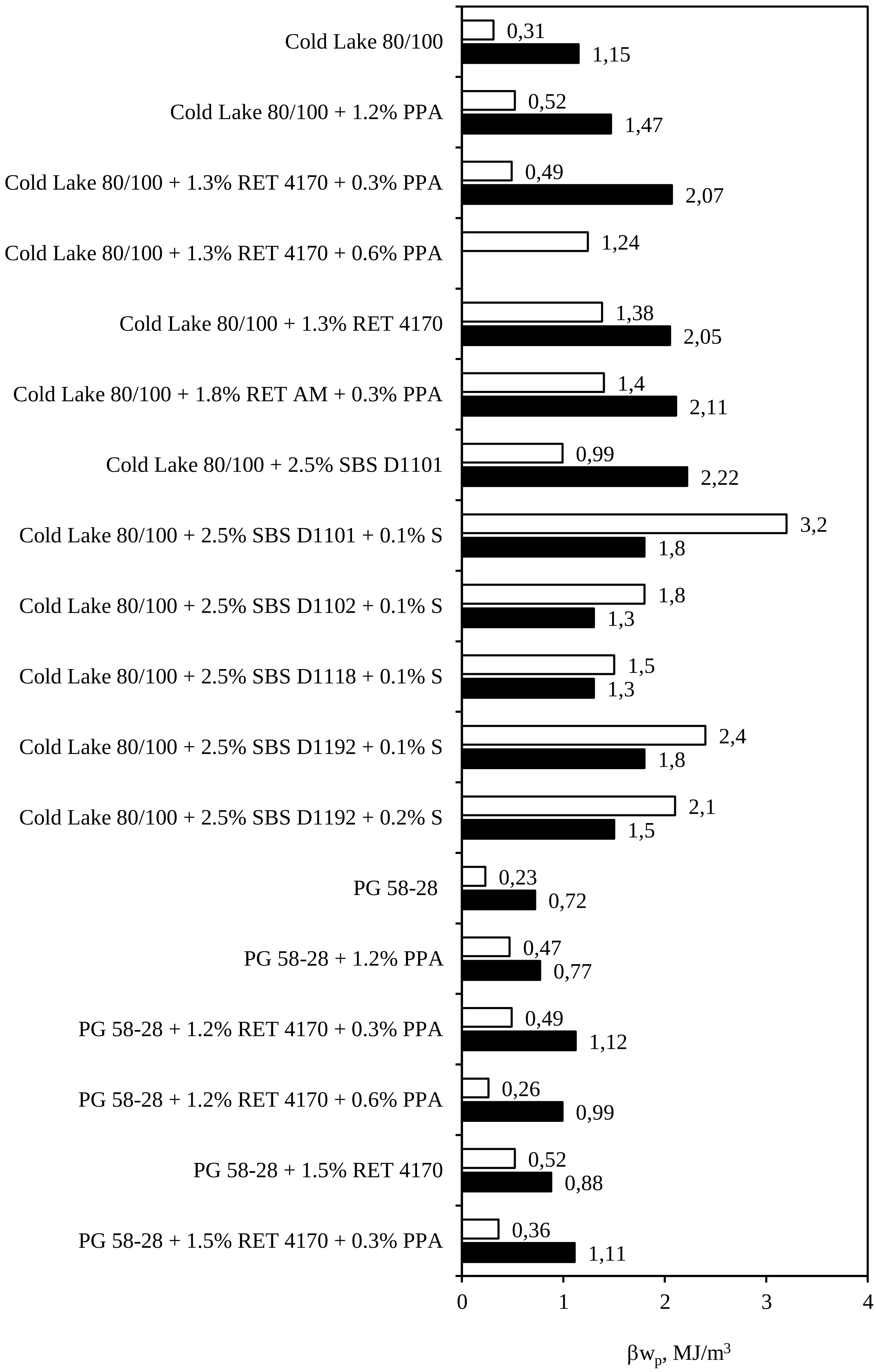

Figure 5 – Plastic works of failure terms for all straight and modified bitumens. *Note:* Open bars are for RTFO residues and filled bars are for the PAV residues. The PAV residue for Cold Lake bitumen modified with 1.3% RET and 0.6% PPA gelled during reheating and hence could not be tested.

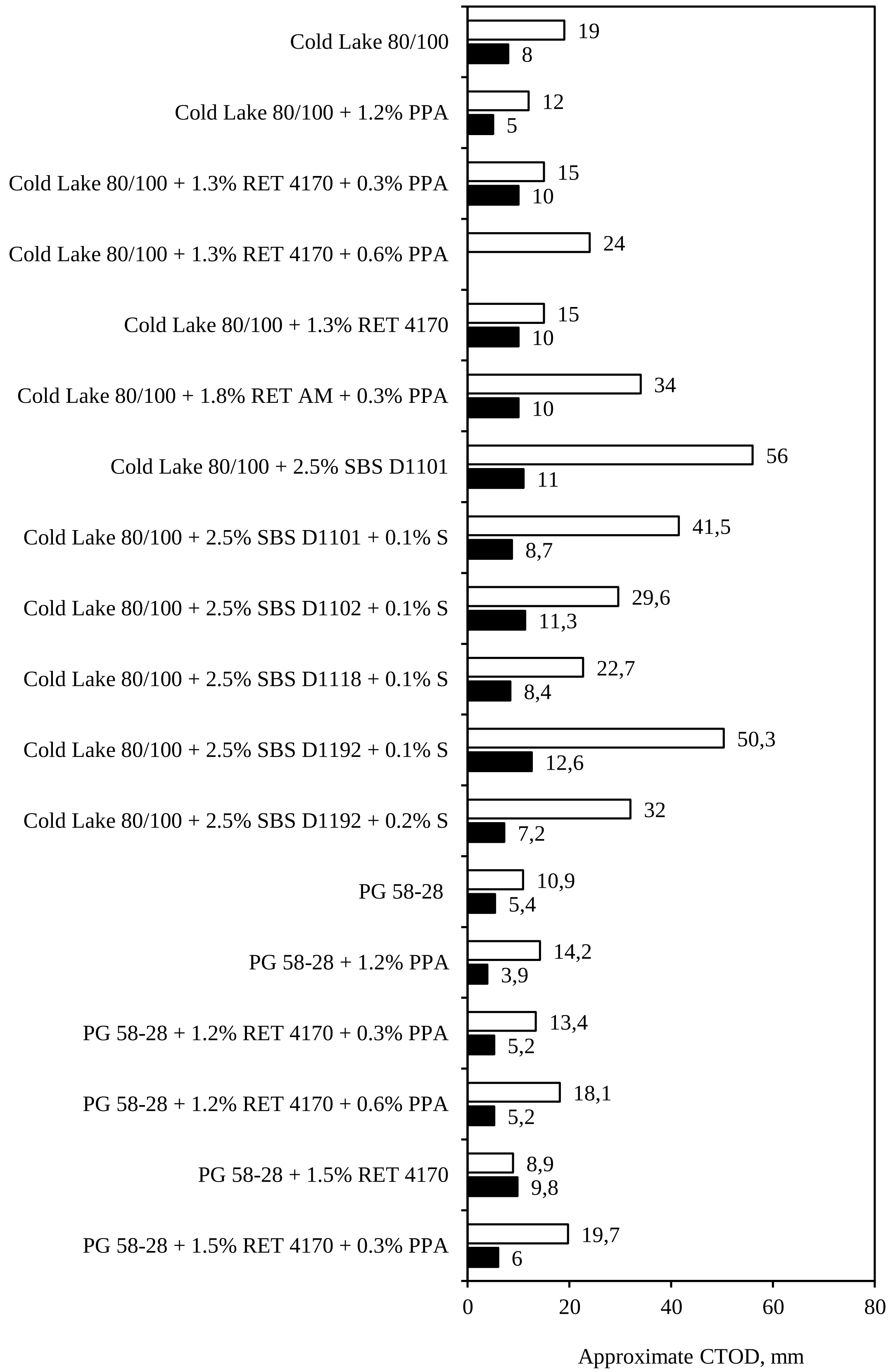

Figure 6 – Critical crack tip opening displacements for RTFO- and PAV-aged bitumens. *Note:* Open bars are for RTFO residues and filled bars are for PAV residues. The PAV residue for Cold Lake bitumen modified with 1.3% RET and 0.6% PPA gelled during reheating and hence could not be tested.

To further support these conclusions, it is worthwhile to briefly review the insights obtained from two pavement trials in northeastern Ontario. The first trial was constructed in 2003 and was exposed to record low surface temperatures of -48°C in 2004 [15]. The pavement reached the design value of -34°C on two occasions. The trial design consisted of seven sections, each 500 m in length, paved on 3.5 km of Highway 655 north of Timmins, Ontario. All variables commonly known to affect cracking performance (voids, VMA, lift thickness, etc.) were kept within tight limits and the only differences were the bitumen source and modification (quality) [15, 33-35].

Figure 7 provides 2011 crack counts versus the initial Superpave grades as determined on the PAV residue (filled symbols) and versus the recovered grades (open symbols) [33, 35]. The data show that RET plus PPA modified bitumen used in Section 1 is outperforming all the SBS modified bitumens of Sections 2-6. The data also show that the Superpave specifications are unable to control cracking. Superpave ranks all the PAV residues approximately the same, and the limiting temperatures are all below the -34°C reached in early 2004. In contrast, the performance has varied dramatically, with Section 1 largely free of cracks and Section 4 in serious need of repairs.

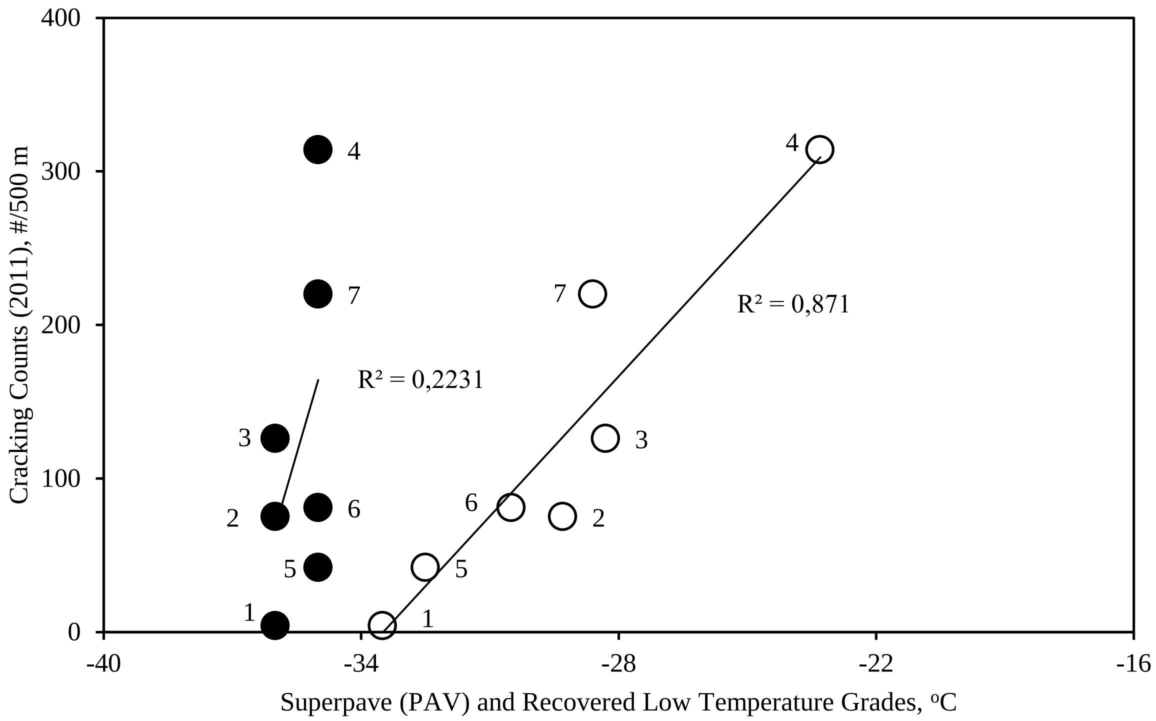

Figure 7 – Cracking distress versus Superpave PAV (filled symbols) and recovered (open symbols) low temperature grades [33, 35]. *Note:* Section 1 = RET + PPA; Section 2 = Ox + SBS; Section 3 = SBS; Section 4 = SBS + WEO; Section 5 = SBS; Section 6 = Ox + SBR + PPA or H_3PO_4; and Section 7 = WEO.

It is apparent from the recovered grades that the observed variations in cracking can be explained by differences in chemical aging. Six of the bitumens were obviously under-designed for thermal cracking due to deficiencies in the RTFO/PAV and/or the bending beam rheometer (BBR) conditioning protocol [15, 33-35]. Hence, this trial may not provide a good validation site for the DENT test, as the method was specifically developed for straight fatigue performance ranking. Nevertheless, the CTOD results for the PAV and recovered residues are able to rank the materials in good order, with materials from Sections 1 and 5 outperforming those for Sections 2-4, 6, and 7 [15].

A second trial was constructed in 2007 on the same highway in order to provide a better site for the DENT test validation and to compare the relative benefits of various bitumen modifiers. The base bitumen used for all eight sections was from Cold Lake. Modifiers included PPA, RET, SB diblock, SBS triblock, and polyethylene terephthalate fibres. The weather since 2007 has been mild so only a single crack has appeared in the section for Cold Lake modified with 7% linear SBS. It is expected that this trial will provide additional validation support for the DENT test in years to come.

4. SUMMARY AND CONCLUSIONS

Given the findings of this research, the following summary and conclusions are offered:

- PPA appears to reduce both the essential work of failure and the CTOD of the bitumen in the ductile state, while RET and SBS appear to increase these properties.
- The benefit of SBS modification on ductile failure properties appears to be much reduced after PAV aging.
- The base bitumen's tendency towards chemical aging (hardening) appears to be of more significance to the ductile failure properties than the nature of the polymer modifier at the modification levels investigated.
- Polymer modifiers at the dosage levels investigated likely provide significant improvements in rut resistance at elevated temperatures but may contribute less to fatigue and low temperature thermal cracking resistance.
- Small changes in additive content will likely have a more significant effect on failure properties than the differences between the various polymer modifiers.

How PPA, RET, and SBS affect the base bitumen performance is of importance to user agencies. Hence, this issue is currently being investigated with a significant number of well-controlled Ontario pavement trial sections.

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DISCLAIMER

None of the sponsoring agencies necessarily concurs with, endorses, or agrees to adopt the findings, conclusions, or recommendations either inferred or expressly stated in subject data developed in this study.

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