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Physical Hardening in Asphalt Mixtures

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Abstract: This paper documents and discusses the physical hardening phenomenon in asphalt mixtures and the implications for pavement performance. Physical hardening can broadly be defined as the gradual stiffening of a material during isothermal storage at low temperatures brought about by changes in structure (wax crystallization, asphaltene aggregation, volume relaxation) rather than chemical composition (volatilization, exudation, oxidation). Seven asphalt mixtures from an eastern Ontario trial on Highway 417 were tested in single-edge-notched tension (SENT) configuration at -22°C after one hour, 24 hours, and 72 hours of conditioning at -10°C. Decreases in the crack mouth opening displacement at peak load ($CMOD_p$) were used to quantify the reduction in strain tolerance in the presence of severe constraint (notches). Increases in the crosshead displacement at peak load (CD_p) were used to assess global damage (microcracking) during conditioning and subsequent testing. After 72 hours of conditioning at -10°C, the changes in $CMOD_p$ ranged from -16% to -56%, whereas changes in CD_p varied from +23% to +223%. The absolute $CMOD_p$ correlated well with performance for this trial, with three poor-performing mixtures showing significant and early cracking in service. These results provide evidence that isothermal conditioning can induce microcracking with simultaneous losses in strain tolerance in the presence of severe constraint (notches), which likely contributes to thermal cracking in service.

Key words*: Asphalt cement; Physical hardening; Specification grading; Thermal cracking.*

Introduction

The physical hardening phenomenon has been well documented for asphalt cements, with regular contributions to the subject published following the pioneering work by Traxler and coworkers in the 1930s [1-3]. A common finding in asphalt cement studies is that stiffness can increase significantly during isothermal storage at low temperatures. It has generally been accepted that volume relaxation due to slow crystallization and/or asphaltene aggregation can cause asphalt cement to lose its ability to deform [1-13].

Far fewer studies have investigated the physical hardening phenomenon in asphalt mixtures. However, till now such studies have failed to provide consistent evidence that this process is detrimental for pavement performance [14-17]. It is likely that some of these studies were confounded by the difficulties associated with laboratory tests on mixtures. Unrestrained mixtures show a tendency to shrink upon isothermal conditioning at low temperatures over extended periods [18]. However, some studies have hypothesized that high thermal shrinkage stresses under restraint can effectively negate the physical hardening process [19, 20]. Yet others have shown with low temperature experiments on mixtures that microcracks can form due to the differential thermal contraction between aggregate and mastic, thus providing an alternate mechanism for reducing the restraining stress [21].

In our view the disagreement in opinions is largely due to a lack of well-designed experiments. Tests in the laboratory on asphalt cement and mixture specimens are not often able to replicate the exact mechanisms that account for cold temperature cracking. Hence, in recent years we have focused our attention on the study of a large number of pavement trials and regular contracts [22-28]. These investigations have shown with a high level of consistency that physical hardening can be an important and frequent contributor to premature and excessive thermal cracking in service.

The long-term objective of our work is to promote the implementation of improved low temperature asphalt cement specification tests that consider the physical hardening phenomenon. These efforts have resulted in the publication of double-edge-notched tension and extended bending beam rheometer (BBR) test standards in the Ministry of Transportation of Ontario's Materials Testing Manual [29, 30]. In the extended BBR protocol the asphalt cement is conditioned at low temperatures prior to testing for periods of one hour, 24 hours, and 72 hours. The associated specification criteria limit the maximum grade loss after 72 hours of conditioning compared to the one hour results and the actual grade after 72 hours of conditioning is required to meet the low temperature grade for the contract location. These criteria will promote the use of superior crude sources and modification technology to provide asphalt cements with lower tendencies for thermal cracking.

This study addresses the outstanding issue of whether physical hardening occurs in asphalt mixtures and to what extent it can impact performance. A series of single-edge-notched tension (SENT) tests were done to separate global microcracking from localized hardening around the tip of a deep notch (simulated pavement flaw) [31]. The SENT results provide a measure of thermal cracking resistance. This approach provides an improvement over the insights obtained from the thermal stress restrained specimen test that is known to be fraught with difficulties [32].

Background

Physical Hardening in Asphalt Cement

The literature on physical hardening has been reviewed in a number

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of recent reports and papers by one of the authors [23, 25-28]. Hence, what follows is a brief summary of the most pertinent contributions.

In 1916 Hubbard and Pritchard [33] documented and discussed their investigation of factors affecting the penetration test on asphalt cements. They found that isothermal conditioning time is one of the controllable variables with significant importance. The authors noted that a gradual hardening occurs as the conditioning time is increased beyond 24 hours.

In the 1930s Traxler and coworkers [1-3] were the first to publish more extensive experimental findings on the phenomenon that asphalt consistency can increase substantially with isothermal storage time. They measured the viscosity of various asphalt cements at room temperature and found significant increases with time. Traxler and Coombs [2] attributed the hardening effect to a “gradual isothermal sol-gel transition.” These early studies revealed that air blown asphalt cements were particularly prone to this process, likely due to their relatively high content of unstable asphaltenes.

In the 1950s Brown and coworkers [4] conducted creep tests in tension and found that the stiffness could increase for periods of days and months. They conducted most of their experiments at room temperature but clearly stated that the effect was relevant under a much wider range of temperatures, times, and conditions.

In 1959 Blokker and Van Hoorn [5] coined the term “physical hardening” for reversible processes that involved wax crystallization and asphaltene aggregation. They commented that both processes were slow at the typically high viscosities and low temperatures and that asphaltene aggregation was able to continue for weeks and months.

In 1990 Pechenyi and Kuznetsov [8] showed that the “formation of partially ordered structures which do not achieve the perfection characteristic of crystals” is largely responsible for the observed hardening. They also commented that by taking into account the phenomenon “it is possible to more reliably and precisely select bitumen of the required structures and viscosity to ensure their maximum durability.”

In 2000 and 2002, respectively, Dongré [19] and Shenoy [20] concluded from experimental and theoretical considerations that physical hardening can be cancelled out by stress relaxation. Dongré [19] studied four different asphalt cements that were fixed at 90 percent of their failure strain and subsequently relaxed for 24 hours. The experiments revealed that while isothermal conditioning increased the thermal stress after 10-24 hours, this increase was reduced to what the author described as an insignificant level in all binders. Dongré [19] and Shenoy [20] questioned the need for a report on physical hardening and suggested that more investigation was needed on asphalt mixtures in which the binder is restrained.

In contrast to these two reports, our own research has shown that significant differences in asphalt cement stiffness and relaxation ability exist after isothermal conditioning. Such differences correlate well with observed performance differences in controlled pavement trials and regular contracts [22-28, 34]. For the Lamont C-SHRP trial the correlation between cracking distress and bending beam rheometer (BBR) properties after three days of conditioning improved greatly compared to the correlation after only one hour of conditioning [23]. In a study on binders recovered from a series of 20 eastern and northern Ontario contracts, those that had cracked prematurely and excessively all lost more than 3°C during three days of isothermal conditioning at -10°C, while those that lost less than 3°C all remained virtually free of cracking distress for periods of 8-16 years of service.

Physical Hardening in Asphalt Mixtures

There are far fewer publications on the physical hardening phenomenon in asphalt mixtures compared to those for asphalt cement. Furthermore, the recent asphalt mixture literature is divided on whether physical hardening is important or just a curiosity that occurs in the cement with little relevance to the mixture in service.

In 1937 Lee and Markwick [35] considered the creep response under both bending and shear loading conditions for asphalt mixtures that were stored for periods of up to 90 days at 25°C. Creep rate decreased dramatically, and this was thought to be due to “complex changes in the physical properties of the binders which occur with time.” The authors felt that the subject was “of considerable practical importance in road construction.”

In 1987 Deme and Young [36] stated that measurements on solvent-recovered asphalt cements from the Ste. Anne Test Road in Manitoba indicated that low temperature stiffness shows little change over five years of service, which was at odds with the steady increase in low temperature cracking over that period. In contrast, the stiffness of the mixture specimens cut from the road showed an increase at all temperature levels, which the authors attributed to “age hardening” or “structural hardening” effects, distinct from chemical aging.

In the 1990s El Hussein and coworkers published a series of studies on the effect of differential thermal contraction in asphalt mixtures at low temperatures [21]. The authors noted that asphalt mixtures lose stiffness when stored at low temperatures due to gradual microcracking at the asphalt mastic-coarse aggregate interface. While the authors did not specifically invoke physical hardening to explain their results, they noted that maximum damage occurred after extended periods of exposure to cold temperatures.

In 1999 Romero et al. [14] presented a study on the physical hardening effect for two SHRP core binders, AAM-1 and AAM-2, which they considered to be particularly susceptible to the physical hardening effect. The authors studied the failure of these asphalts at low temperatures by utilizing the thermal stress restrained specimen test (TSRST) on mixtures prepared with two different aggregates. They were able to show a significant decrease in performance with only one of the asphalts. However, physical hardening data were not provided for the actual binders used, and the paper was silent on the fact that there was a considerable difference in wax content for the two materials investigated, with only the higher wax content showing a significant change in TSRST performance as measured by the failure temperature.

More recent papers by Lu et al. [15] and Soenen et al. [16] documented and discussed results for 20 different straight and modified asphalt mixtures in the TSRST and failed to note significant changes due to isothermal storage. However, Soenen et al. [16] did find a significant increase in mixture stiffness due to isothermal conditioning.

It is our opinion that this discord in opinions is largely due to the difficulties involved with the TSRST on asphalt mixtures [32]. Fig. 1 shows data published by one of the authors regarding a cyclic cooling test on a specimen just above and below the damage threshold of around -22°C [32]. It is obvious that at a critical temperature, the specimen starts to sustain damage, as is evident from the reduction in peak stress in each consecutive cooling cycle. It is also clear that thermal damage accumulates gradually over a period of days. Hence, restrained cooling tests such as those performed by the above-mentioned groups were likely confounded by the presence of simultaneous physical hardening and microcracking.

Materials and Methods

Materials

Asphalt cements were obtained from the sampling valve on the pipeline feeding directly into the hot mix plant during the construction of each individual test section. They were collected in the summer of 2006 on the eastbound lanes of Highway 417 between Limoges and Casselman in eastern Ontario. The pertinent properties of the seven asphalt cements are provided in Table 1. The seven materials were obtained from four different commercial sources in Canada and the United States. The low temperature grades requested from each supplier was a PG-34, although two of the materials actually ended up grading as a PG-40. The base asphalt for three of the binders came from Alberta (likely Cold Lake and/or Lloydminster sources) while the base for the remaining four binders remains unknown.

Asphalt mixture samples were obtained during the construction of each individual test section during late summer of 2006 and were stored in 20 kg boxes until further use in the fall. Three batches of loose mix were heated in an oven set at 180°C for two hours, mixed with a bucket mixer for approximately one minute, followed by heating for an additional one hour, and finally compacted into slabs measuring 40 cm × 60 cm × 15 cm of approximately 72 kg each. The convection oven took considerable time to reach the set point of 180°C after samples were loaded. Mix temperatures were monitored periodically and the compaction temperatures for all slabs ranged between 120°C and 130°C. The hot mixture was spread evenly in the cavity of a custom made laboratory slab compactor where it was slowly compacted to the target void content of 7.0 %. After cooling, prismatic specimens of 154 mm × 130 mm × 48 mm were cut with a diamond-tipped cutting saw to a precision of ± 1 mm from the center of each slab. The outside edges of each slab were discarded to assure constant voids for all specimens. Samples were attached to aluminum end blocks with high strength epoxy glue. Finally, the specimens were notched to a depth of 40 ± 1 mm, and knife edges were glued on the mouth opening in order for a clip-on gauge to be attached for the measurement and control of the CMOD.

Table 2 provides pertinent end result specification data, as well as the average voids contents for the seven slabs tested as measured by weighing above and under water.

Methods

Asphalt cements were aged according to standard RTFO and PAV methods and graded according to regular AASHTO M320 protocols [37] as well as Ontario’s double-edge-notched tension (DENT) and extended BBR standard tests, LS-299 [29] and LS-308 [30], respectively.

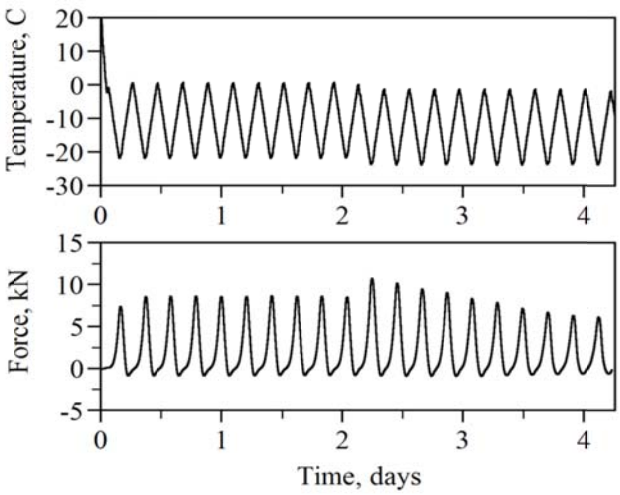

Fig. 1. Thermal Fatigue Cycles on Asphalt Mixture Sample [32]. *Note*: First ten cooling cycles incurred no damage while second ten cycles were just below the damage threshold of -22°C.

Table 1. AASHTO M320 Grading Results for Asphalt Cements.

Section	AASHTO M320 Grade, °C
417-1	64-34
417-2	70-34
417-3	82-40
417-4	70-34
417-5	64-40
417-6	76-34
417-7	64-34

Note: All asphalt cements were highly modified. Modifiers for this trial included reactive ethylene terpolymer (RET) with polyphosphoric acid (PPA), styrene-butadiene-styrene (SBS), and unknown additives. Grades were determined from pass/fail tests after 1 hour of conditioning at the test temperature and are rounded to the nearest 6°C. The required Superpave® grade for the trial area is PG 64-34. The binders were obtained from four different commercial sources.

The LS-299 method specifies the pulling of asphalt cement specimens in a double-edge-notched tension (DENT) configuration to failure [29]. Notch depth in the samples varies to provide ligament lengths (L) of 5 mm, 10 mm, and 15 mm in a test specimen 30 mm wide and 10 mm thick. The rate of elongation is kept constant at 50 mm/min and the temperature is kept constant at 15°C.

The area under each load-displacement curve is measured to determine the total work of failure, W_f, which comprises an essential and a non-essential part, $W_{essential}$ and $W_{non-essential}$. The total work is divided by the ligament cross-sectional area (L × B) to determine the specific total work of failure (w_f). This specific work is then plotted versus the ligament length, L, and the intercept of the plot provides the essential work of failure, w_e, according to Eqs. (1) and (2):

Table 2. Asphalt Mixture Properties from End Results Specification Tests and Slab Analysis.

Section	Surface Course (ERS)		Binder Course (ERS)		Slab
	Air Voids, %	Compaction, %	Air Voids, %	Compaction, %	Air Voids, %
417-1	3.8	93.7	4.0	93.5	7.5
417-2	4.4	93.2	3.9	93.7	6.9
417-3	4.4	94.7	4.2	92.9	7.1
417-4	4.4	94.6	4.8	93.5	6.7
417-5	4.6	94.3	4.2	93.5	7.0
417-6	4.1	92.8	4.5	94.2	6.7
417-7	3.7	92.7	4.0	93.2	6.8

Note: Air voids were determined according to standard methodology by weighing dry, wet but surface dry, and under water. Results are averages for three individual QC/QA plate and core samples. End result specification (ERS) tests were done shortly after the construction of the trial during the summer of 2006. Air voids for slab specimens were determined shortly after compaction during the fall of 2006.

$$W_f = W_{essential} + W_{non\text{-}essential}$$
$$= w_{essential} \times L \times B + w_{non\text{-}essential} \times \beta \times L^2 \quad (1)$$

$$w_f = W_f/LB = w_{essential} + \beta w_{non\text{-}essential} \times L \quad (2)$$

where:

W_f is the total work of failure, J (area under the force versus displacement curve)

$W_{essential}$ is the essential work involved in forming the new failure surfaces, J

$W_{non\text{-}essential}$ is the non-essential or plastic work away from the failure zone, J

$w_{essential}$ is the specific essential work of failure, J/m^2

$w_{non\text{-}essential}$ is the specific non-essential work of failure, J/m^3

L is the ligament length, m

B is the specimen thickness, m

β is a scaling factor that describes the shape of the plastic zone around the failure plane.

The essential work is then divided by the average peak net section stress for the 5 mm ligament specimens, σ_{5mm}, in order to calculate an approximate critical crack tip opening displacement, CTOD [29]:

$$CTOD = w_e/\sigma_{5mm} \quad (3)$$

This approximate CTOD (m) provides a measure of strain tolerance in ductile failure. It should be realized, however, that the CTOD can vary a great deal with temperature, rate of loading, and age. Hence, the LS-299 specification criteria are meant to exclude very poor performers rather than to provide a perfect correlation with cracking distress.

The LS-308 specification test method [30] and associated criteria provide a simple extension of the regular BBR as embodied in the AASHTO M320 specification [37]. The BBR beams are conditioned for periods of one hour, 24 hours and 72 hours at temperatures above the pavement design temperature which is obtained from the LTPPBind® software. The absolute grade after three days needs to meet the contract requirement, and the grade loss is limited to a maximum depending on the conditioning temperature. It is anticipated that these criteria will promote the use of superior crude sources and modification technology to provide asphalt cements with lower tendencies for thermal cracking.

Asphalt mix specimens were conditioned at -10°C for periods of one hour, 24 hours and 72 hours prior to testing to failure at -22°C. The conditioning and test temperatures were selected based on the conditions experienced at the Highway 417 test site in eastern Ontario. The lowest pavement temperature measured at the site was -22°C during early 2007. All SENT specimens were equilibrated at the test temperature for 45 minutes prior to the start of testing in an MTS 810 servo-hydraulic test frame equipped with an environmental chamber. The specimens were loaded in uniaxial tension at a relatively fast crack mouth opening displacement rate of 20 μm/min to failure.

Pavement distress was surveyed during Spring 2007 and Summer 2010, and approximate transverse crack lengths were calculated for each 500 m test section.

Results and Discussion

Asphalt Binder Testing

The DENT (LS-299) results for the PAV residues are provided in Fig. 2. The figure shows that the ductile strain tolerances of the asphalt cements, as measured by the approximate critical crack tip opening displacement (CTOD), vary by a modest degree, with sections 417-1 through 417-3 outperforming sections 417-4 through 417-7. The observed differences are described as modest since experience has shown that certain polymer modified binders can give CTODs as high as 40 mm or even 50 mm [27]. Further, variations in chemical aging tendencies in service can easily change the relative rankings. Finally, the strain tolerances also change with temperature due to variations in hardening tendency, and this will certainly have an effect on performance in service. Performance differences for binders of the same Superpave® grade can easily be explained by differences in chemical and physical hardening that are not captured by a single test at 15°C [26, 27, 29]. Hence, LS-299 is meant to exclude very poor performers rather than to provide a perfect correlation with cracking distress.

The extended BBR (LS-308) results are provided in Fig. 3, which shows that the physical hardening tendencies for these asphalt cements are modest, as judged by their AASHTO M320 criteria after isothermal conditioning. Average three day grade losses for all sections are 3.2°C, 3.4°C, and 4.0°C after conditioning at -10°C, -20°C, and -30°C, respectively. Such losses are considered small since experience has shown that truly inferior asphalt cements (i.e. those modified through harsh air blowing, paraffin wax

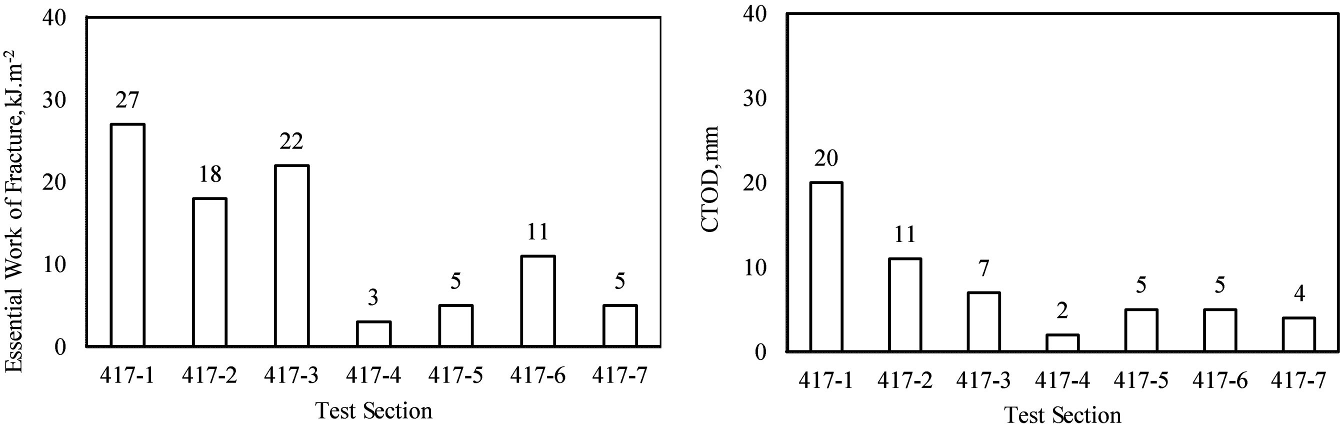

Fig. 2. (a) Essential Works of Fracture for Asphalt Cements; and (b) Approximate Critical Crack Tip Opening Displacements for Asphalt Cements (T = 15°C).

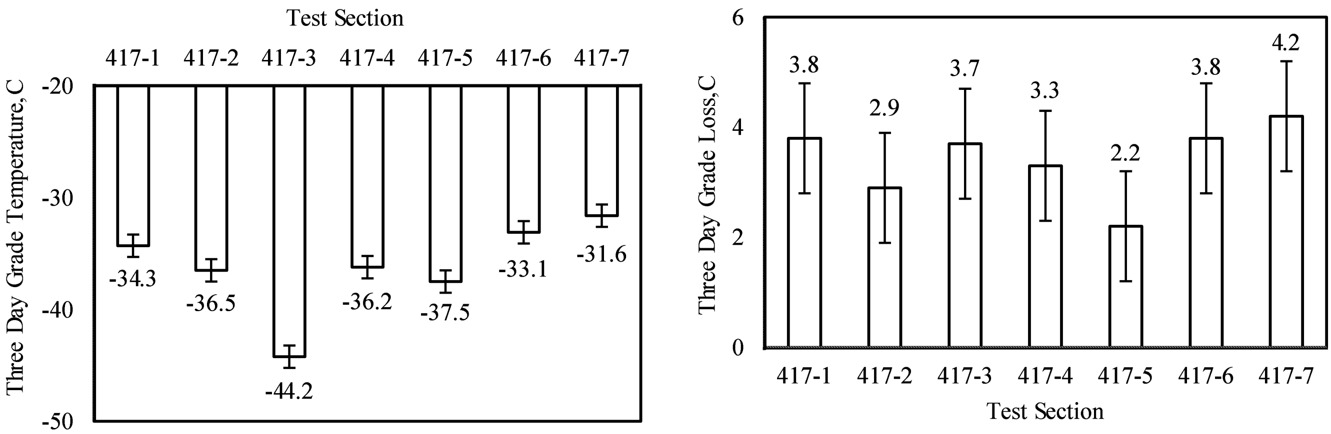

Fig. 3. Extended BBR Test Results: (a) Absolute Grade after Three Days Conditioning at -20°C; and (b) Grade Loss after Three Days of Conditioning.

Note: Error bars provide approximate standard deviation as obtained from round robin testing.

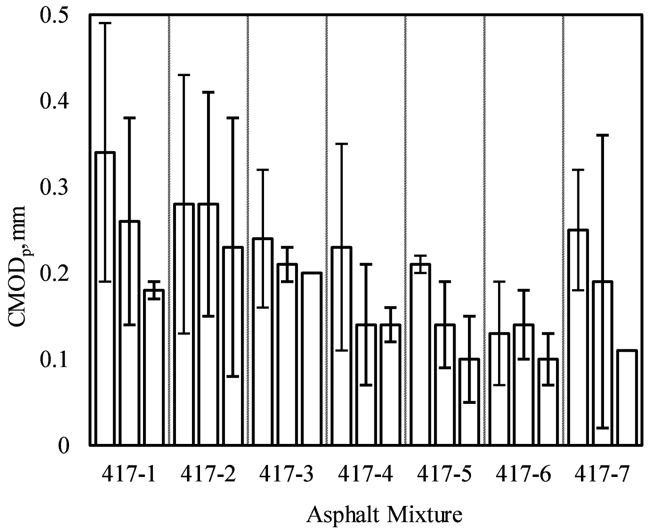

Fig. 4. Crack Mouth Opening Displacements at Peak Load after Various Conditioning Times.

Note: Tests were conducted at -22°C after 1 hour (first column), 24 hours (second column) and 72 hours (third column) of conditioning at -10°C. The $CMOD_p$ consistently decreases with increased conditioning time.

modification, waste engine oil modification, etc.) can lose as much as 6°C to 12°C [22, 23, 25, 27, 28].

Asphalt Mixture Testing

Fig. 4 provides the crack mouth opening displacement ($CMOD_p$) at peak load after various conditioning times. The results show that these findings are consistent with significant physical hardening as is evident from the reduction in $CMOD_p$ as isothermal conditioning time increases. Decreases in the $CMOD_p$ range from -16% (Section 417-3) to -56% (Section 417-7). Hence, these findings provide evidence that physical hardening effects can be very significant in asphalt mixtures. Therefore, the physical hardening effect is a likely contributor to early and excessive cold temperature cracking in northern pavements. Whether the same differences will be observed at lower rates of loading typical for asphalt mixtures in service can likely only be determined from actual field trials, since such experiments in a laboratory test frame would become exceedingly time consuming and thus costly.

The hardening effects as observed in these asphalt mixtures appear to be more severe than what was found for the corresponding asphalt cements (Fig. 3). However, the cement properties were

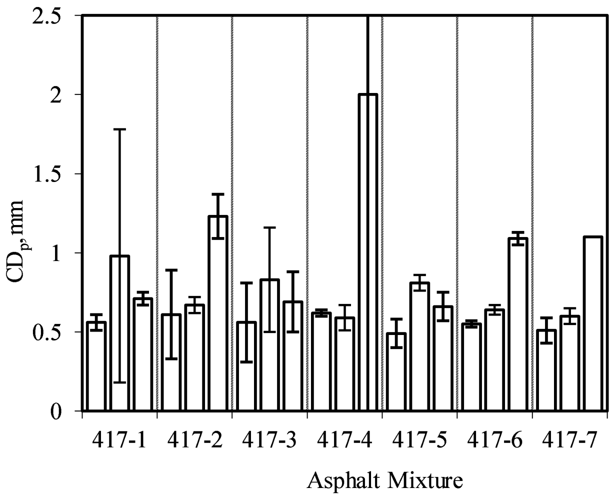

Fig. 5. Crosshead Displacements at Peak Load after Various Conditioning Times.

Note: Tests were conducted at -22°C after 1 hour (first column), 24 hours (second column) and 72 hours (third column) of conditioning at -10°C. The CD_p largely increases with increased conditioning time.

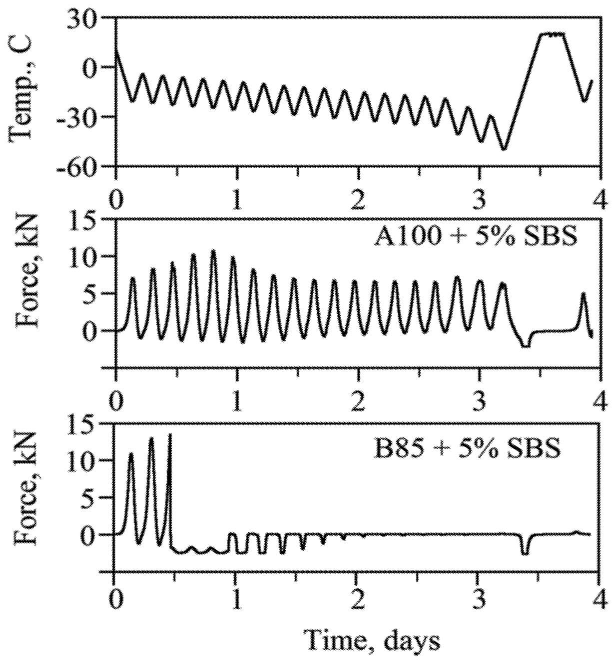

Fig. 6. Thermal Fatigue Cycles on Asphalt Mixture Samples [32].

Note: Sample A had a low asphaltene content while sample B had a relatively high asphaltene content.

determined on PAV residues, while the mix samples were taken during construction and reheated in the laboratory for compaction. Further, the mixture tests are those at a constant CMOD rate, while the data in Fig. 3 were obtained in creep tests on slender cement beams. Thus, comparing asphalt cement with mixture tests is not entirely straightforward.

Fig. 5 provides the crosshead displacement at peak load (CD_p). The general increase in CD_p is consistent with a reduction in stiffness due to global microcracking. Increases in CD_p range from +23% (Section 417-3) to +223% (Section 417-4). This can explain why the TSRST fails to provide meaningful results for the detection of physical hardening in asphalt mixtures. The TSRST is better done on notched samples [32]. Deep and sharp notches reduce the failure stress and hence will localize the damage at temperatures warmer than those reached in unnotched specimens. Such experimental design has a better chance at discriminating the good from the not-so-good materials [32].

In our previous study we found that a particular polymer modified asphalt cement with little asphaltene content showed far superior performance in thermal fatigue compared to a second material with higher asphaltene content (see Fig. 6) [32]. The asphaltene rich material showed more catastrophic failures, which can be due to increased levels of physical hardening. Field studies with similar materials have also shown a reduced tendency for physical hardening and subsequent thermal distress [28].

Pavement Condition Surveying

The pavement distress was measured for the entire length of each 500 m test section in Spring 2007, Spring 2008 and Summer 2010. In 2007 there was no noticeable distress in any of the test sections.

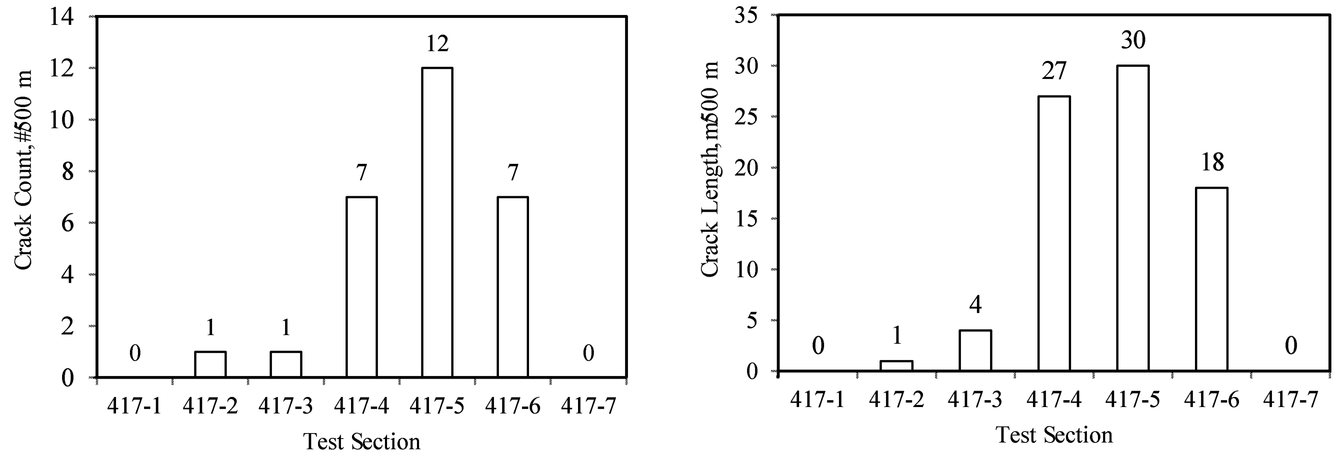

Fig. 7. Pavement Distress for Summer 2010: (a) Number of Cracks for Each Section; and (b) Total Crack Length for Each Section.

Note: These data indicate that the trial is still young with relatively few cracks.

In 2008, only 14 m of transverse cracking was observed in Section 417-5. Fig. 7 provides a summary of the 2010 findings and shows that Sections 417-1 through 417-3 and 417-7 remain largely free of thermal distress, and Sections 417-4 through 417-6 are significantly damaged due to low temperature exposure.

These findings are largely in agreement with the asphalt cement and mixture results presented above. Differences in performance for trial sections of identical Superpave® grades can likely be explained by differences in chemical and physical hardening tendencies of the asphalt cement. The only anomaly for this trial is that Section 417-7 has remained largely free of distress. This test section is located about 2 km away from the other six sections, and hence the subgrade could be slightly different. Another reason for the inconsistency could be that this trial is relatively young in age, and thermal cracking will likely increase in a few years.

Conclusions

Given the results presented in this paper, the following summary and conclusions are provided:

- Isothermal storage of asphalt mixture samples reduces the strain tolerance at low temperatures, as was revealed by significant reductions in crack mouth opening displacement at peak load in a single-edge-notched tension test.
- Isothermal storage appears to significantly increase the crosshead displacement at peak load during tensile testing, which can be explained by possible microcracking due to differential thermal contraction at the coarse aggregate interface.
- The strain tolerance as quantified by the crack mouth opening displacement at peak load appears to correlate reasonably well with the resistance of an asphalt mixture to thermal cracking distress.
- Differences in strain tolerance for binders of the same Superpave® grade can likely be explained due to variations in chemical and physical hardening tendencies.

Given the encouraging findings of this study, it appears that the time has come to include physical hardening protocols in current asphalt cement specifications.

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Disclaimer

None of the sponsors necessarily concurs with, endorses, or has adopted the findings, conclusions, or recommendations either inferred or expressly stated in the subject data developed.

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