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GLASS TRANSITION MEASUREMENTS OF ASPHALTS BY DSC

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Abstract

The glass transition temperature (T_g), measured by Modulated Differential Scanning Calorimetry (MDSC), is related to the flow characteristics of asphalt at low temperatures as is the rate of change of the creep stiffness *m*. This study compared the glass transition temperature of different asphalts (neat, chemically modified, and crumb rubber modified asphalts) with the creep stiffness, the rate of change of creep stiffness, and the low specification temperature of the continuous PG grading of those asphalts.

From the rheological data (BBR) and the thermal data (MDSC) for the virgin and the modified asphalts, the modified products had the same variations of values of *m*, *S*, and T_g at lower temperatures as those of their corresponding virgin asphalts. A correlation between the T_g and *m* value was observed for both the modified and unmodified asphalts. Since DSC measurements for asphalt low temperature properties use less operator time, less sample, and have less measurement and operator error than rheological methods, T_g has promise to be considered as a fast and easy laboratory method to obtain the low temperature useful range of asphalts in pavements.

Keywords: asphalt, creep stiffness, glass transition, rheology

Introduction

The viscoelastic nature of asphalt plays a very important role in the performance of asphaltic pavements at both high and low temperatures. Presently, the Strategic Highway Research Program (SHRP) has created a protocol by which low temperature properties of asphalt, creep stiffness *S* and rate of change of creep stiffness *m* are measured by a Bending Beam Rheometer (BBR); and the medium and high temperature properties, the fatigue factor $G^{*}\times\sin\delta$ and rutting factor $G^{*}/\sin\delta$, are measured by the Dynamic Shear Rheometer (DSR).

Thermal analysis is a tool which can measure different parameters, heat flow directions, heat capacity, melting transition, crystallization, glass transition temperature, etc., of polymers and other organic materials. Asphalt is a mixture of different compounds, and its thermal behavior is completely dependent on those different complex materials. Such *et al.* [1] reported that thermal behavior of an asphalt binder is completely dependent on its thermal history. The highly crystallized asphalts have shown higher limiting stiffness with different rheological behaviors [2]. Kumari [3] reported that the enthalpy of crystallization is dependent on thermal history of asphalt. Glass transition is dependent in part on the wax content of asphalt

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as reported by Bahai *et al.* [4]. The thermal behavior of SHRP core asphalts is reported by Caudy *et al.* [5]. The thermal behavior of Superpave core asphalts studied using DSC, it was observed that thermal history has a significant influence on the thermal behavior of asphalt [6].

Materials and preparation

Superpave asphalts AAD-1 (PG 58-28), AAV (PG 52-28) and AAG-1 (PG 58-10) were used for this study. Crumb rubber of mesh size -80 (CRM-4) was used and was supplied by Rouse Rubber Industries Inc., Vicksburg, MS. All reagents used were of HPLC grade from Baxter Scientific Products, McGraw Park, IL. Furfural Modified asphalt (FUMA) was prepared according to the work reported by Chollar *et al.* [7]. Crumb rubber modified asphalt (CRMA) was prepared as reported by Memon *et al.* [8].

CRMA material preparation

Laboratory reactions were run at 163°C by heating 234 g of asphalt (AAD-1 or AAG-1) in a round bottom flask to the above specified temperatures, followed by the addition of 35.1 g of crumb rubber (15%). The mixture was heated for 3 h at that temperature in continuous stirring mode.

Analytical instruments used

1) TA Instruments Inc. Modulated Differential Scanning Calorimetry (MDSC).
2) Cannon Bending Beam Rheometer (BBR).

Experimental

Thermal characterization

Low temperature data for the neat, CRMA, and FUMA were obtained by MDSC. A CRMA sample was placed in a stainless steel cup (open cup with lid), and the material was heated to about 80–90°C to create a homogeneous thin film at the bottom of the cup. The cup was sealed, placed in the MDSC's sample compartment, and cooled to –125°C. It was left at that temperature for 15 min to create a standard thermal history in the sample and then heated to 70°C at a rate of 1°C min^{-1} with oscillating amplitude of 5 cycles per 60 s. This procedure was repeated for crumb rubber (CRM AAD-1, CRM AAG-1), the furfural modified asphalt (FUM AAV, FUM AAD-1), and neat asphalts (AAD-1, AAG-1, and AAV). The reversing, non-reversing, and heat capacity signals for these materials were measured.

Low temperature hehavior by BBR

A Cannon bending beam rheometer (BBR) was used to determine the low temperature rheological behavior of virgin and crumb rubber modified asphalts. Samples were run in triplicate at –24, –18, –12°C, and S and m were determined by using the standard AASHTO procedures for asphalt AAD-1 and its modified (furfural and crumb rubber) product.

Results and discussion

Strategic Highway Research Program (SHRP) has developed the performance PG grading system for both high and low temperatures and replaced the conventional penetration and viscosity methods used for grading the asphalt. The Superpave PG grading is based on the rheological behavior of asphalt for both high and low temperatures. High temperature PG grading is mainly derived from the loss compliance in extension or flexure ($G^*/\sin\delta$). Low temperature PG grading is derived from low temperature rheological properties: mainly from flexure creep stiffness S, which is actually the inverse of the creep compliance; and from the rate of change of creep stiffness m, obtained from the slope of the log of creep stiffness *vs.* log of time (Fig. 1). It was observed that due to time temperature superposition, and in order to keep a reasonable testing time (60 s), the low temperature data observed at 60 s is 10°C higher than the actual temperature at which the pavement may thermally crack.

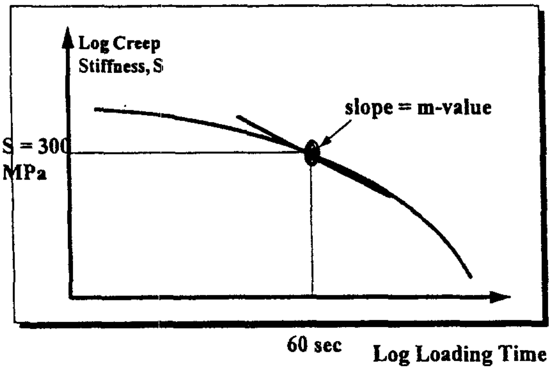

Fig. 1 Creep stiffness of asphalt

In order to obtain low temperature rheological properties of asphalts for the SHRP PG grading system, the asphalt specification suggests the use of BBR. Sample preparation for BBR needs much effort and time. It requires a two step asphalt aging procedure, i.e., rolling thin film oven test (RTFOT) aging at 163°C for 80 min (simulating drum dryer mix conditions of the asphalt and aggregate), and pressure aging vessel (PAV) aging of the RTFOT aged samples at 100°C at 300 psi (simulating 5 to 10 years of aging of asphalt in the pavement) (Fig. 2). It is observed that bending beam rheometer can give an error of 4–7%. Asphalts subjected to these conditioning procedures have not showed any problems; however, modified binders subjected to these aging processes may show problems of inhomogeneity af-

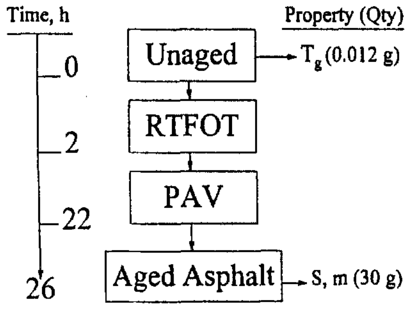

Fig. 2 Laboratory asphalt aging process

ter RTFOT conditioning due to improper rolling and high viscosity. Modified binders may also undergo possible unwanted interactions during PAV aging.

Both m and S are related to the flow characteristics of asphalt and are indicators of the susceptibility of asphalt to low temperature cracking. The glass transition (T_g) is the temperature range at which a change of material from a glassy to rubbery state occurs. It is related to the flow characteristics of an asphalt. T_g also indicates the susceptibility of asphalt to thermal or low temperature cracking. Modulated differential scanning calorimetry (MDSC) can provide this desired information from DSC curves by differentiating reversing and non-reversing profiles of the DSC curve, which separates and identifies cold crystallization and the hysteresis peak of the glass transition (a non-reversing heat flow event) from T_g (a reversing event). The results obtained through MDSC are very repeatable.

Figure 3 is DSC curve showing the repeatability of the instrument. The figure shows two curves of asphalt AAG-1. The T_g in both curves are very close, meaning that MDSC is very repeatable.

Figures 4 and 5 are plots of rate of change of creep stiffness m and creep stiffness S *vs.* T_g (heating rate 3°C min^{-1}) for neat asphalts (AAA-1, AAB-1, AAC-1, AAD-1, AAF-1, AAK-1 and AAM-1), showing r^2 values of 0.76 and 0.89 respectively.

Figures 6 and 7 are plots for neat and modified asphalts (with furfural and crumb rubber) showing the correlation factors for m and s *vs.* T_g (heating rate 1°C min^{-1}) of 0.95 and 0.89 respectively.

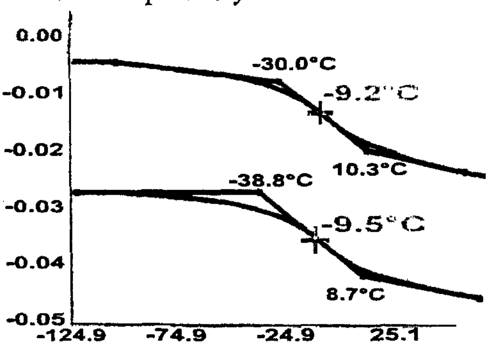

Fig. 3 Repeatability of asphalt AAG-1 by MDSC

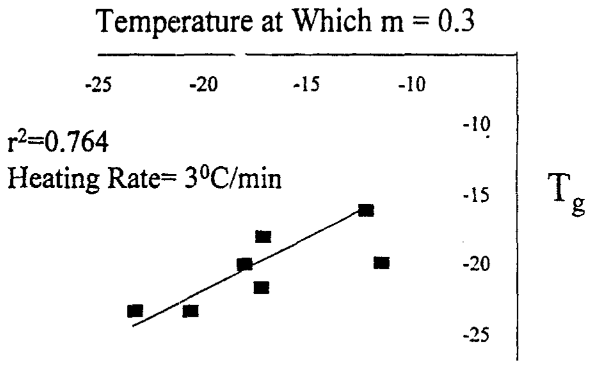

Fig. 4 *m vs.* T_g of neat asphalts

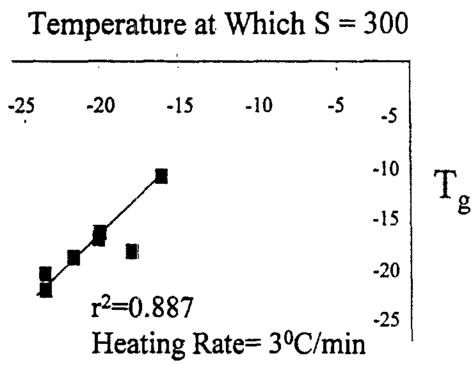

Fig. 5 *S vs.* T_g of neat asphalts

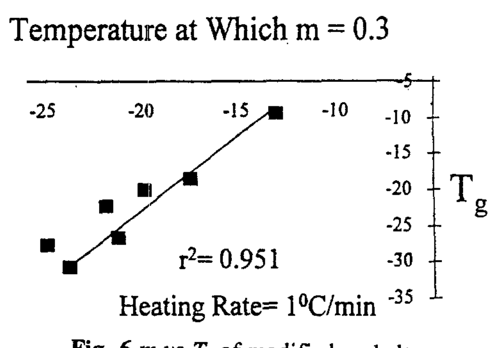

Fig. 6 *m vs.* T_g of modified asphalts

The r^2 data in Figs 4–7 show that heating rates of 1 °C min^{-1} for determining the T_g of asphalts provide a better and more reliable correlation of low temperature rheological properties with T_g than data collected with higher rates.

Although these data show trends of a relation between low temperature rheological properties and T_g, more work with a larger group of asphalts is needed.

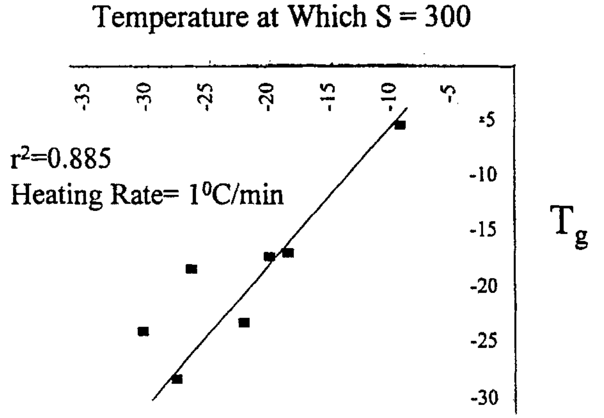

Fig. 7 S *vs.* T_g of modified asphalts

Conclusions

* T_g from MDSC data is repeatable.

* Correlation of rheological properties (both rate of change of creep stiffness m and creep stiffness S) for neat and modified asphalts is in reasonable agreement with T_g (heating rate 1 °C min^{-1})

* Correlation of low temperature rheological properties (both m and S) for neat asphalts is in the right direction with T_g (heating rate 3 °C min^{-1})

* This thermal procedure is a fast and easy way to characterize the low temperature properties of asphalt.

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