THE GLASS TRANSITION TEMPERATURE AND THE MECHANICAL PROPERTIES OF ASPHALT

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This is an advance copy of a paper to be presented at the Annual Conference of the Canadian Technical Asphalt Association (536 Broughton Street, Victoria, British Columbia) to be held in Halifax, Nova Scotia, October 30 - November 1. This advance copy is primarily to stimulate discussion. Discussion is invited and may be transmitted to the Chairman. The paper is subject to modification and is not to be published in whole or in part pending its release by the Association through the Chairman.

Introduction

During recent years transverse and longitudinal cracking of flexible pavements in cold weather regions has led to a greater interest in the mechanical properties of asphalt at low temperatures. The study of the mechanical behavior of asphalt at low temperatures has introduced a term into the asphalt literature which will undoubtedly be examined in greater detail during the coming years. This property of asphalt is termed the glass transition temperature (Tg). The glass transition temperature, widely used in polymer science, is defined as the temperature at which there is a change in slope in the specific volume-temperature curve (see figure 1).

It is termed a second order transition in order to distinguish it from the melting point (m.p.) which is a first order transition. In figure 1 it is the point at which the rate of change of specific volume with respect to temperature undergoes a discontinuity. Mack (1) refers to the glass transition as the temperature below which the translatory motion of molecules has ceased. Below the glass transition temperature, asphalt is in a glassy

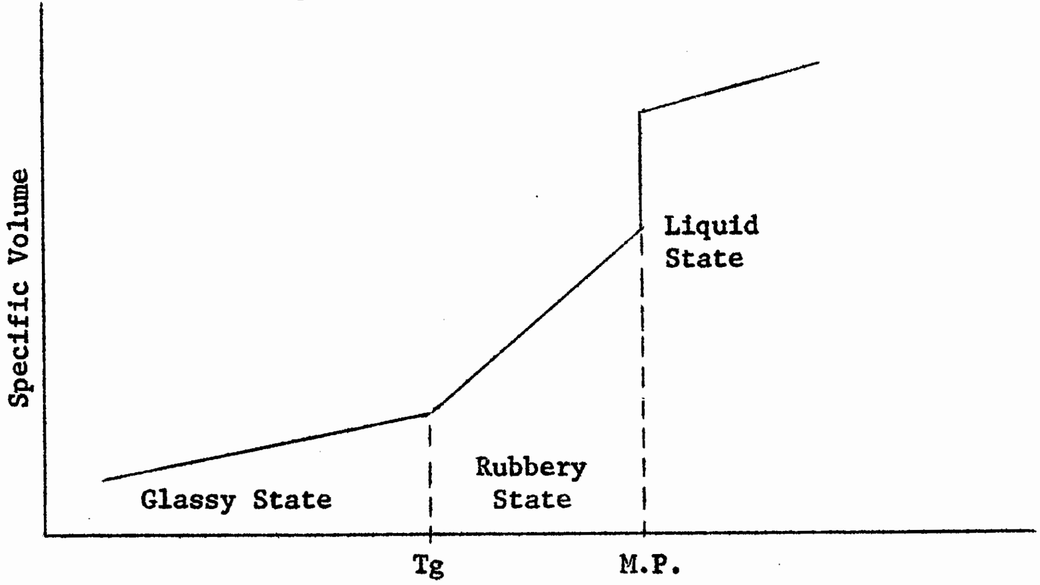

FIGURE 1

state and above its behavior is viscoelastic. A technique for measuring the glass transition temperature of asphalt has been developed by Schmidt and Santucci (2). Schmidt (3) also has reported that there is a possible relationship between high glass transition temperature of the asphalt and transverse crack frequency in pavements. Although further study is needed in this area, factors that may influence the value of the glass transition and its relationship to low temperature mechanical behavior need to be examined.

The Glass Transition Temperature and the Degree of Polymerisation

In order to develop an understanding of what controls the glass transition temperature, a review of some work in the area of high polymers is presented. Although asphalt is not a pure polymer, Barth (4) suggests that there is evidence for the opinion that the high molecular weight hydrocarbons in asphaltenes can be physically termed a pseudopolymer with the linkage of hetroatoms connecting a monomer of simpler structure.

A polymer is obtained by building large molecules from small monomer or repeat units. The number of these units that are linked together is termed the degree of polymerisation of the polymer. The molecular weight of the polymer molecule can be expressed as

$$\text{Molecular Weight} = (\text{Mo})\ (\text{DP})$$

where Mo is the molecular weight of the monomer and DP is the degree of polymerisation. In a real polymer, however, all molecules will not have the same number of monomers, and what results is a material that has a molecular weight distribution similar to that shown in figure 2.

As a further example, in 3000 molecules of a polymer there may be 2,000 molecules with a DP of 100 and 1000 molecules with a DP of 10. In order to describe the material then, statistical characteristics of the distribution must be used. The mean and standard deviation of the DP would then be characteristics of the distribution. Fox and Flory (5) found when working with polystyrenes that the glass transition temperature was related to the degree of polymerisation of the polymer. High glass transition temperatures correlated well with high degree of polymerisation as indicated by average molecular weight of the material.

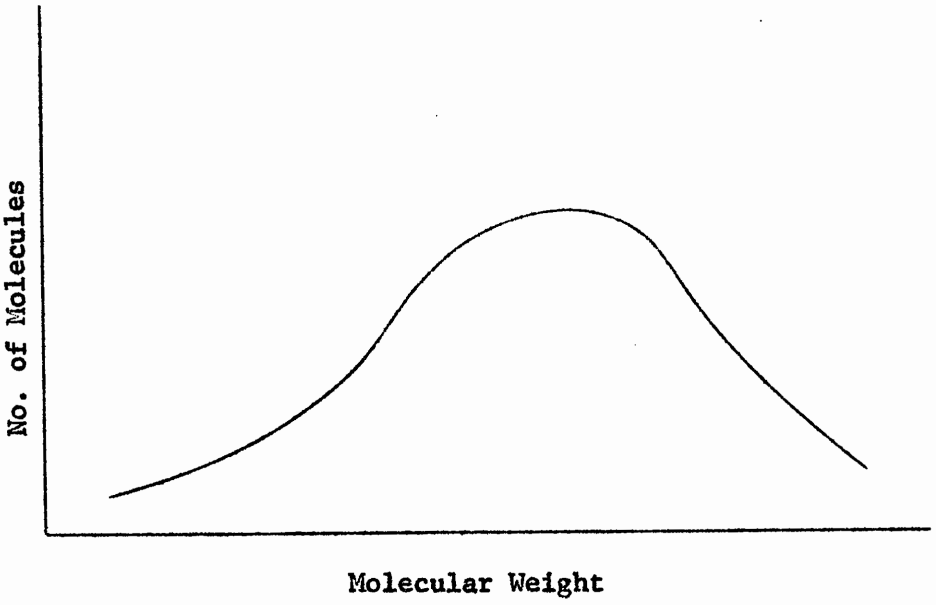

Figure 2

Figure 3 shows the effect of the degree of polymerisation on the glass transition temperature.

Although the characteristics of the monomer that make up the polymer will influence the glass transition temperature, it has been shown for a given monomer unit, the higher the degree of polymerisation, the higher the glass transition temperature.

Figure 4 illustrates a hypothetical molecular weight distribution curve for an asphalt. Richman (6) describes techniques for obtaining such curves by means of Gel Permeation Chromotography.

The molecular weight distribution curve is divided into three zones of different molecular weight ranges; the oils, resins, and asphaltenes. If the asphalt is considered as a pseudopolymer with the oil fraction being the monomer unit, then the asphaltenes will have the highest DP and the resins an intermediate DP. For a given asphalt then, it would be expected that the higher the asphaltene and resin content, the higher the glass transition temperature. Schmidt (2) in his paper before the AAPT

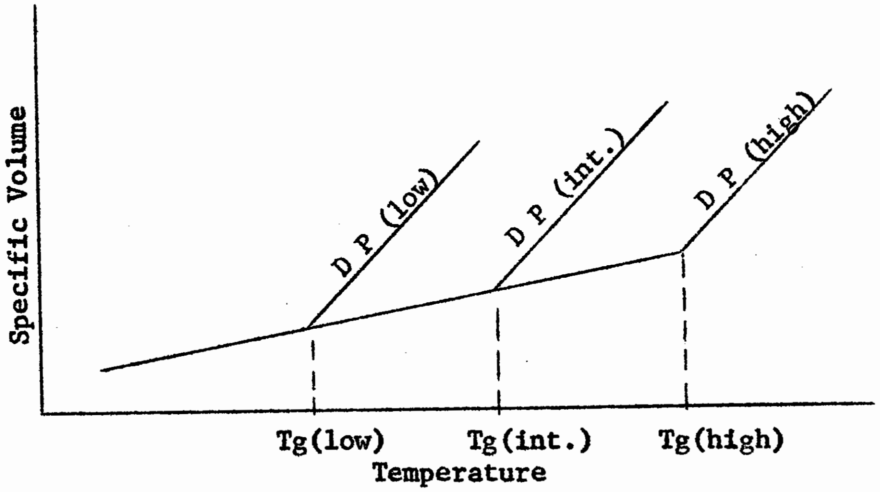

FIGURE 3

stated that for a given crude source, the lower penetration, the higher the glass transition temperature. Assuming penetration is inversely related to the degree of polymerisation, his work bears out the influence of the degree of polymerisation of the asphalt on the glass transition temperature.

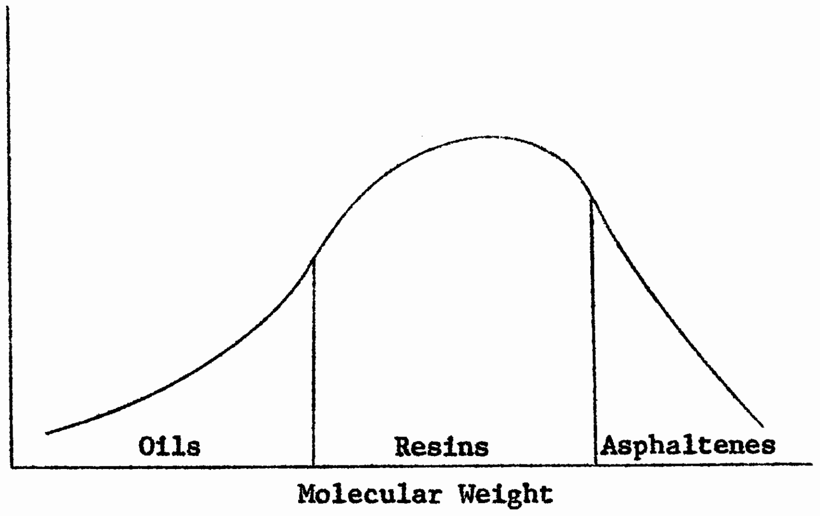

FIGURE 4

Mechanical Properties

In order to predict the behavior of an asphalt pavement at low temperature, more than one test will be required. As was mentioned earlier, Schmidt (3) reported to the AAPT that there is a possible relationship between the glass transition temperature and transverse crack frequency with high crack frequency being associated with a high glass transition temperature. In his research, Schmidt used the glass transition temperature as the characteristic temperature for applying the principle of corresponding states in analyzing viscosity data. Recent research by Moavenzadeh (7) on determining the fracture properties of asphalt has led to a possible conflict as to the value of the glass transition temperature in predicting mechanical cracking tendencies. Table I, II, and III contain a summary of data that is available on two asphalt cements that are being tested under the Asphalt Institute, Bureau of Public Roads Cooperative Research by Welborn, Oglio and Zenewitz (8), Halstead, Rostler and White (9), Schmidt and Santucci (2) and Moavenzadeh (7). The two asphalts are coded as B-2960, an 85-100 penetration grade asphalt and B-3056, a 30 penetration grade. B-2960 has a glass transition temperature of -20.2°F and B-3056 a glass transition temperature of -1.3°F. From the data, it can be seen that B-2960 has a viscosity of 106 megapoises at 39.2°F, .05 sec^{-1} shear rate and B-3056 has a viscosity of 495 megapoises under the same test conditions. From Moavenzadeh's data, the 30 penetration grade asphalt is much stiffer at 0°F having a modulus of elasticity of 95, 100 p.s.i. compared to a 30,600 p.s.i. for the 85-100 penetration grade asphalt. Since the 30 penetration asphalt has a high glass transition temperature, the higher viscosities and stiffnesses (E) are as expected. The strain energy release rate G_c at 0°F for the 85-100 asphalt is .0242 in.-lb/in^2 compared to .0195 in.-lb/in^2 for the 30 penetration asphalt. The greater tendency for cracking of the 30 penetration asphalt implied by the higher transition temperature is not substantiated by these release rates.

The effects of aging on brittleness for the two asphalts tested is shown in Tables II and III. The 85-100 penetration asphalt had a change in weight of 11 percent and an increase in its modulus of elasticity from 30,000 p.s.i. to 38,300. The 30 penetration asphalt showed an increase in modulus from 95,100 p.s.i. to 104,100 p.s.i. However, there is a major change in their strain energy release rate. The 85-100, which is more age susceptible, lost 11% weight, increased 25% in stiffness and had a gain in strain energy release rate of 140% from .0242 in-lb/in^2 at zero hours aging to .0583 in-lb/in^2 at 6 hours aging. In comparison, the 30 penetration is not age susceptible as weight and strain energy release rate remain constant and stiffness increased by only 8%. There is no data available on the effect of aging on the glass transition temperatures.

The ductility data for the two asphalts appears to present a different picture, the 85-100 penetration asphalt with its lower glass transition temperature does have a higher ductility at 5 cm/min 45°F compared to the 30 penetration grade asphalt, 11 compared to 3. Since the value of the ductility test in predicting brittleness is open to discussion, the exact meaning of these values is in doubt. However, if the ductility is used as a criterion for brittleness, the glass transition temperature measurements do predict that the 30 penetration asphalt has a lower ductility than the 85-100 penetration asphalt at failure.

A low glass transition temperature does not relate stiffness (E) with brittleness as measured by the strain energy release rate. A crack susceptible asphalt will then have to be defined by more than one parameter, possibly including the strain at failure, strain energy release rate, fatigue, and aging characteristics of the asphalt.

Conclusions

Although data is available for only two asphalts as reported in the literature, it is apparent that the glass transition temperature will be used in predicting low temperature cracking in the future. As has been pointed out, low glass transition temperature does not necessarily mean that the asphalt is crack susceptible, as its susceptibility may be a function of its strain energy release rate. The glass transition temperature, when used in conjunction with molecular weight characteristics and mechanical tests, may point out the mechanism that controls cracking of pavements at low temperature. Also as far as the structural design of asphalt pavements is concerned, the load distributing characteristics of the pavement will be affected by the stiffness of the bound layers. If the pavement layer is near its glass transition temperature, it may be resisting applied wheel loads predominately by beam action.

Asphalt source is probably another variable that affects the glass transition temperature just as the characteristics of the monomer unit in polymers affects their glass transition temperatures.

The effects of aging on the glass transition temperature and strain energy release rate is a problem that is in need of further research. Hopefully by knowing these quantities, it will be possible to select asphalts that will not be crack susceptible at low temperature.

Acknowledgement

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TABLE I

Characteristics of Viscosity - Graded Asphalt Cements

BPR LABORATORY NUMBER	B-2960	B-3056
Viscosity 275°F	482 cs	430
Viscosity 140°F	2060 poise	2684 poise
Viscosity 77°F, .05 sec^{-1}	1.41 mp	12.5 mp
Viscosity 60°F, .05 sec^{-1}	10.5 mp	82.0 mp
Viscosity 45°F, .05 sec^{-1}	57. mp	394 mp
Viscosity 39.2°F, .05 sec^{-1}	106. mp	495 mp
Penetration 100 gms 5 sec. 45°F	14	3
Penetration 100 gms 5 sec. 60°F	32	11
Penetration 100 gms 5 sec. 77°F	87	30
Ductility 1 cm/min 45°F	62	3.5
Ductility 5 cm/min 45°F	11	3
Ductility 5 cm/min 60°F	161	10
Ductility 5 cm/min 77°F	160	250+

TABLE II

Characteristics of Residues from Thin Film Oven Test

BPR LABORATORY NUMBER	B-2960	B-3056
Change in Weight %	-11	-.05
Penetration 77°F	56	24
Ductility 5 cm/min 77°F	159	137
Ductility 5 cm/min 60°F	15	4
Viscosity 140°F	5479 poise	5300 poises
Viscosity 275°F	749 cs	564 poises
Viscosity 60°F, .05 sec^{-1}	32 mp	115 mp
Retained Penetration %	64.4	80.0

TABLE III

Mechanical and Chemical Properties

BPR LABORATORY NUMBER	B-2960	B-3056
Glass Transition Temperature	-20.2°F	-1.3°F
Modulus of Elasticity (E) @ 0 hrs aging 0°F	30,600	95,100
Modulus of Elasticity (E) @ 6 hrs aging 0°F	38,300	104,100
Strain Energy Release Rate G_c @ 0 hrs aging 0°F	.0242	.0195
Strain Energy Release Rate G_c @ 6 hrs aging 0°F	.0583	.0149
% Asphaltenes 0 hrs aging	26.23	15.83
% Asphaltenes 6 hrs aging	34.15	20.03
Asphaltenes (A)	27.9	19.2
Nitrogen Bases (N)	12.0	21.0
First Acidaffins (A_1)	24.4	27.3
Second Acidaffins (A_2)	25.6	18.3
Paraffins P	10.1	14.2
$\frac{N+A_1}{P+A_2}$	1.02	1.49
Pellet Abrasion @ 77°F, % loss	3.0	83.0

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