

## CURRENT PRACTICES FOR MODIFICATION OF PAVING ASPHALTS

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### Introduction

The Superpave binder specification, AASHTO MP1 (1), has introduced new concepts for selecting paving asphalt binders. The specification, in addition to using rheological and failure measurements that are more related to performance, is based on the idea that the criteria to maintain a satisfactory contribution of asphalt binders to the resistance of pavement failures remains the same but have to be satisfied at critical application temperatures. The test procedures require that the material be characterized within certain ranges of strains or stresses to ensure that material and geometric nonlinearities are not confounded in the measurements.

These new specification concepts have resulted in re-evaluation of asphalt modification by the majority of modified asphalt suppliers. The philosophy of asphalt modification is expected to change, following these new concepts, from a general improvement of quality to more focus on using modifiers based on the most critical need as defined by two factors:

- The application temperature domain
- The type of distress to be remedied

The new specification requirements should result in a more effective use of modifiers as the amount and type of modifier will be directly related to the application environment and the engineering requirements.

### Modification to meet the Superpave Binder Specifications

The Superpave binder specification parameters have been selected such that one or more material properties are used to evaluate the potential contribution of asphalt binders to resistance of critical pavement distress types (2,3):

**Workability:** Rotational viscosity is used as the indicator of workability. This is a requirement that is not related to climatic conditions, but is necessary to ensure that binders are workable enough so that mineral aggregates can be properly coated and asphalt mixtures can be compacted efficiently to reach the required density.

This requirement is critical for many modifiers currently used because they tend to increase in consistency and thus result in less workability. To achieve required workability, temperatures for mixing and compaction are usually increased. This can result in increased production cost, more volatile loss, increased oxidative aging, and possible degradation of certain modifiers.

**Permanent Deformation:** Complex shear modulus ( $G^*$ ) is used as the indicator of total resistance to deformation (rigidity) under cyclic loading. Sine of the phase angle ( $\sin \delta$ ) is used as the indicator of relative elasticity of the binder under cyclic loading. Both parameters are combined in the parameter ( $G^*/\sin \delta$ ) to ensure that the binder will have acceptable contribution to resistance of permanent deformation.

This requirement indicates that modification of asphalts, to resist permanent deformation, can be done either by increasing rigidity, elasticity, or both. Rigidity is a material characteristic that is much easier to alter because of the nature of the asphalt. Rigidity can be increased by oxidation in the refinery process, by using low cost additives that will work as inert fillers, or by using stiffeners that will react with asphalt and change its consistency. Elasticity, on the other hand, requires creating an elastic structure using certain types of elastomeric materials. These materials, mostly polymeric in nature, should exhibit compatibility with the asphalt and be resistant to changes due to oxidation, phase separation, and unstable reaction. Elasticity has been identified as an important property needed to improve pavement performance. This concept is based mostly on few pavement tests sections and accelerated failure tests in the laboratory. How much elasticity is needed, and what is the elastic structure's contribution to the resistance to permanent deformation, is difficult to quantify. In the Superpave specification the parameter  $\sin \delta$  was selected based on the concept of dissipated energy. It is derived with the consideration that asphalts are compared within the linear visco-elastic region. This has important ramifications for some modifiers because their elastic response is different at different strain or stress levels. Strain dependency is discussed in a following section.

**Fatigue Cracking:** Same parameters ( $G^*$  and  $\sin \delta$ ) are used as the indicators of resistance to fatigue cracking. An important distinction is that the specification targeted only strain controlled fatigue as the main fatigue distress. The whole Superpave system (binder and mixture) does not focus on stress controlled fatigue. Using the same energy concepts, the parameter  $G^*\sin \delta$  is used to indicate that resistance to strain-controlled fatigue can be achieved by decreasing rigidity ( $G^*$ ) and/or increasing elasticity (lower  $\sin \delta$ ).

From a modification perspective, decreasing rigidity (measured by  $G^*$ ) is simpler than increasing elasticity. Rigidity can be decreased in the refining process, by using fluxing agents, or with other low cost hydrocarbons that are compatible with asphalts. Increasing elasticity requires the same basic modifications discussed earlier in relation to permanent deformation. It is, however, more complex at intermediate temperatures because most asphalts show a significant amount of elasticity at intermediate temperatures. To add more elasticity, a highly elastic structure created by an elastomer is needed. The same complications discussed in regard to the strain dependency apply at intermediate temperatures. Unmodified asphalts have a narrow range of linear visco-elastic behavior at intermediate temperatures. In the nonlinear range unmodified asphalts show tendency to lose their elastic behavior (increase in  $\delta$ ) differently than asphalts modified with elastomeric materials. This difference can result in dissimilar performance of modified asphalts in the non-linear range.

**Low Temperature Thermal Cracking:** Because of the important role of the binder in thermal cracking, the Superpave specification includes three parameters that are combined in any one parameter. Creep stiffness,  $S(@60\text{sec})$ , is used as an indicator of the amount of thermal stresses that can be built in the asphalt due to a given thermal gradient induced strain induced by temperature change. Logarithmic creep rate,  $m(@60\text{sec})$ , is an indicator of the relative elasticity; higher  $m$  (60) values indicate less elasticity and more ability to relax stresses by viscous flow. Failure strain,  $\epsilon_f$ , is used as an indicator of brittleness or the ability to stretch without cracking (strain tolerance).

Modification of low temperature properties can be achieved by changing one or more of these parameters. In most cases it is difficult to use modifiers that will change one of these indicators while keeping the others constant. Unlike fatigue, thermal cracking indicators favor modification that results in less elastic binders. This should be easier to achieve since refining processes and additives that result in softer binders either reduce or do not affect the elasticity (higher  $\delta$  and higher  $m$  values). Strain tolerance can be increased by many several mechanisms. Elastomeric polymers can improve strain tolerance. Plastomers and certain fillers can work as crack arresters and increase strain tolerance. Certain hydrocarbons, because of their low glass transition temperature, can significantly improve strain tolerance.

#### Types and Amounts of Modified Asphalts

There is a large number of modifiers used in paving applications at the present time. In a survey published in 1993 (4), there were a total of 48 commercial brands of asphalt modifiers. These modifiers were classified in 5 classes including 10 fillers/extenders, 16 thermoplastic polymers, 3 thermosets polymers, 1 liquid polymer, 4 aging inhibitors, and 10 adhesion promoters. During the Strategic Highway Research Program (5, 6) 82 asphalt modifiers or modified asphalts were obtained, documented and stored at the Material Reference Library. These 82 sources of modifiers were classified in 8 classes including 39 thermoplastics, 27 anti-stripping agents, 5 anti-oxidants, 2 fibers, 2 extenders, 1 recycling agent, and 1 oxidant. In an internal report by the Engineering Staff of the Asphalt Institute (7), 48 types of modifiers were identified. They were classified into 13 polymers, 10 hydrocarbons, 6 mineral fillers, 6 antioxidants, 6 antistripping additives, 4 fibers, 2 extenders, and 1 oxidant.

The classification of asphalt modifiers can be done based on the composition and physical nature of the modifier, based on the mechanism by which it alters asphalt properties, or based on the target asphalt property that needs to be modified. Table 1 is generated, based on a review of literature (4, 5, 6, 7), to summarize the generic types of asphalt modifiers classified according to the nature of the modifier. The target distress shown in the table is the main distress or property that the additive is expected, or claimed, to affect favorably. The information is based on interpretation of the published information for brands of modifiers that belong to the modifier classes shown. In many cases the reported effects are based on limited data, which means that the effects cannot be generalized to all asphalt and/or aggregate sources.

#### Typical Effects of Modification On Superpave Binder Parameters

A sample of effect of modification on the Superpave Binder parameters is shown in figures 1 to 4. In all these figures the relative changes (modified/unmodified) in the performance indicators are shown. The base asphalts vary among the modifiers but not for a modifier. Figure 1 shows the effects of some elastomeric polymers (SB and SBR). The ratios are calculated using values measured at temperatures for which the base asphalt meets the respective requirements for each of the parameters. As depicted in Figure 1, the elastomeric polymers show favorable effects on all performance related parameters.  $G^*/\sin \delta$  increases,  $G^*\sin \delta$  and  $S(60)$  decrease, and  $m(60)$  and strain at failure increase. The relative changes are however higher for the  $G^*/\sin \delta$  and failure strain than the other parameters.

Figure 2 depicts the changes for another asphalt modified with 3 different plastomeric additives at 4% by weight of asphalt. These vary in their molecular weight but all are polyethylene based. The only significant change is seen at high temperatures for the parameter  $G^*/\sin \delta$ . It appears that these plastomers are not effective with this particular asphalt at intermediate or low temperatures.

Figure 3 depicts the effects of three different types of crumb rubbers. These are all mixed at 15% by weight of asphalt. The effect on the values of  $G^*/\sin \delta$  are more pronounced than the

plastomeric modifiers but the effects on the other parameters are not very significant. These rubbers are not reacted and no extender oils were used in preparation of their mixtures with the asphalt.

Figure 4 depicts the effects of two mineral fillers (C: Calcite and Q: quartz) mixed at 50 % volume concentration. As depicted, these fillers significantly increase  $G^*/\sin \delta$ , which is a favorable effect. They, however, also increase  $G^*\sin \delta$ ,  $S(60)$  and they decrease  $m(60)$ . These effects are not favorable and may contribute to significant increase in fatigue and thermal cracking.

The data presented in Figures 1 to 4 are samples of data collected for specific asphalts. They cannot be generalized for all asphalts. Several of these modifiers/additives react with asphalts and their effects are therefore asphalt specific. They are presented here to give an overview of the general trends of effects. The data clearly shows that the most significant effect is seen at high temperatures in the parameter  $G^*/\sin \delta$ . This is expected since asphalts exhibit the least stiffness at higher temperatures. If the effects on  $G^*$  and  $\sin \delta$  for these modifiers are considered separately, it is clear that the most significant effect is on the value of  $G^*$ . Even for the elastomeric modifiers, the phase angle did not drop by more than 25 degrees. For an asphalt with a phase angle of 80 degrees, this change will only result in a 15% reduction of  $\sin \delta$ . This finding substantiates the concept that it is more difficult to induce elasticity at high temperatures than to enhance rigidity with most of the modification techniques used currently.

#### Characteristics not Considered by the Superpave Binder Specifications and Test Protocols

The Superpave binder specification is based on important assumptions that are justified for unmodified asphalts. Several of these assumptions may not be valid for some modified asphalts. Following are some of the critical assumptions or characteristics that are not considered and which are currently being discussed by asphalt researchers.

**Dependency of viscosity on shear rate:** The rotational viscosity is measured at 135 C at a recommended rate of 20 rpm. This shear rate was selected because most unmodified asphalts show Newtonian behavior (viscosity is independent of shear rate) at this rate. It was also selected to simulate shear rates during pumping and handling in refineries and asphalt plants. Many modified asphalts are highly shear dependent at and above the value of 20 rpm. Modified asphalts can also exhibit elasticity at these high temperatures, which cannot be measured with a viscometer. The current rotational viscosity protocol for Superpave does not include a procedure to measure shear rate dependency and the criteria for workability do not address this characteristic of modified asphalts. In the mixture design requirements of Superpave, it is required to mix at a viscosity of approximately 0.17 Pa-s and compact at 0.28 Pa-s. These low viscosities cannot be achieved for many modified asphalts unless they are heated to extremely high temperatures.

**Strain dependency of rheological response under cyclic loading:** The rheological properties in the Superpave specification are measured at selected strain levels. These strain levels are selected to be within the linear viscoelastic range for unmodified asphalts. The basis for the selection was the relation between limit of linear behavior and the value of  $G^*$ . For modified asphalts it is known that this relation may not hold true. Figures 5 to 7 depict strain dependency of selected modified asphalts. Figure 5 is for an asphalt modified with two polymeric modifiers, including both an elastomeric and a plastomeric modifier. Figure 6 is for an asphalt modified with crumb rubber, and Figure 7 is for an asphalt modified with a rigid filler. In all cases it is apparent that there is a shear thinning effect. The  $G^*$  decreases with strain while the  $\delta$  increases. Unmodified asphalts also show a shear thinning effect; the linearity limit on the strain scale decreases as the temperature decreases. The Superpave specification does not allow for consideration of strain dependency nor does it refer to a range of strains that are typically encountered in the field.

The concept in the Superpave specification is to select asphalts based on their performance within the small strain (linear) range because pavements should not be designed to encounter large strains. In other words asphalts should be compared within the (safe) pre-failure region within which they do not undergo high deformation or stresses. It should be mentioned however that it is very difficult to estimate the true strain distribution in an asphalt-aggregate mixture under loading. It is difficult because of the irregular shape of aggregates and the random distribution of voids and binder between aggregates. For the specification to be applicable for materials that do not show a wide linear region, a range of strains should be defined and used in testing. Strain dependency should not be considered as an inferior property. Strain dependent materials (nonlinear materials) can perform well if their strain/stress dependency is taken into account.

**Thixotropy and effect of mechanical working:** Effect of repeated loading at constant rates on  $G^*$  and  $\delta$  is another behavior that is not considered in the Superpave specifications. Certain additives can result in a thixotropic network structure that can be destroyed or altered by repeated shearing. Such structure can be destroyed permanently by mechanical working or can be affected temporarily and regained when material is left to rest. Not many asphalt modifiers that are currently used are known to show such a behavior. Figure 8 depicts a typical example of a time sweep for an asphalt before and after modification with polymeric additives. The figure shows that neither the  $G^*$  nor the  $\delta$  are changing in this experiment where the asphalts are being sheared at 10 rad/s every 6 seconds for more approximately 66 seconds. Some asphalts modified with Tall oil and some gel-like compounds can show significant changes due to

mechanical working. Similar to strain dependency, thixotropy should not be considered as an inferior material property. If thixotropy is considered properly in testing and evaluation, thixotropic materials can outperform non-thixotropic materials.

**Loading rate dependency:** The testing in the specification is conducted at selected loading rates that are assumed to be typical under traffic on open highways. It is well recognized that traffic does not move at one speed. It is also known that thermal cooling cycles vary significantly in their cooling and warming rates. Dependency on loading rates is material specific, not only for modified binders but also for unmodified asphalts. The testing rate of 10 rad/s used for cyclic testing, and the loading time of 60 seconds used for the creep testing, are based on simplifications of asphalt behavior. Modification may result in nullifying the assumptions used in these simplifications. The effect of modification on loading rate dependency should be considered in selecting modifiers and a more comprehensive procedure should be included in the specification to evaluate this property.

**Time-Temperature Equivalency:** Testing for low temperature creep is done at 10 °C higher than the lowest pavement design temperatures. Also in the guidelines for considering slow moving traffic and traffic amount, it is recommended to shift temperature of testing rather than loading frequency. These requirements and guidelines are based on the assumption that the time-temperature equivalency factors are similar for most asphalts. Although there are similarities in time-temperature equivalency factors for asphalts (8), the equivalency factors can vary for asphalts with different glass transition behavior and asphalts that are heavily modified. One of the common modification techniques is to use softer asphalts with good low temperature properties, and use additives to improve high temperature properties. Such a modified asphalt may have a glass transition region that is significantly lower than an unmodified asphalt with equivalent high temperature properties. These two asphalts can show significantly different time-temperature shift factors due to the difference in transition temperature range. The glass transition region and time-temperature equivalency of asphalts are important properties that are not fully considered in the specifications.

#### Concluding Remarks

The Superpave binder specification introduces a new system that can more accurately evaluate the effect of modifiers on performance related properties of asphalt binders. There is a variety of additives that are used as asphalt modifiers in paving applications. These can be classified based on their composition and/or effects as polymers (elastomeric and plastomeric), fillers, fibers, hydrocarbons, anti-stripping agents, oxidants, antioxidants, crumb rubber, and extenders. A sample of polymers, fillers, and crumb rubber modifiers was evaluated using the Superpave binder tests. The results indicate that they can impart significant changes on the properties measured in the Superpave specification. The main changes they can impart reflect on the rigidity of the binder ( $G^*$ ) at the intermediate to high pavement temperatures encountered in the field.

The testing protocols included in the Superpave specification are not inclusive of certain important characteristics that are typical of modified binders. Among these characteristics are strain dependency, thixotropy, loading rate dependency, and time-temperature equivalency. These characteristics are modifier specific and ignoring them in selecting modifiers may lead to underestimating or overestimating the effect of the modifier on pavement performance. Typical results for strain dependency and mechanical working were presented for a group of selected modifiers. The Superpave specifications should include provisions to measure these characteristics, and guidelines to assess their effects on pavement performance.

#### References

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**Table 1. Generic types of asphalt modifiers currently used for paving applications.**

The classification of CLASS		EFFECT ON DISTRESS				AGN <sup>5</sup>
		PD <sup>1</sup>	FC <sup>2</sup>	LTC <sup>3</sup>	MD <sup>4</sup>	
<b>1. Mineral Fillers</b>	Carbon black	x				x
	Hydrated lime	x				x
	Fly ash	x				
	Portland cement	x				
	Silica fume	x				
	Baghouse fines	x				
<b>2. Extenders</b>	Sulphur	x	x	x		
	Some fillers (baghouse dust)					
<b>3a. Polymers Elastomers</b>	<i>Styrene block copolymers</i>	x	x	x		
	Styrene butadiene diblock (SB)	x		x	x	
	Styrene butadiene triblock/radial block (SBS)	x	x	x		
	Styrene Isoprene (SIS)	x				
	Styrene ethylbutylene (SEBS)					
	<i>Styrene butadiene rubber latex (SBR)</i>	x		x		
<b>3b. Polymers Plastomers</b>	Polychloroprene latex	x	x			
	Polyisoprene (natural and synthetic)	x				
	Ethylene Propylene diene monomer (EDPM)	x				
	Polyisobutylene	x				
	<i>Ethylene vinyl acetate (EVA)</i>	x	x			
	<i>Ethylene methacrylates (EMA)</i>					
	<i>Polyethylene (low density and high density)</i>	x		x		
	Polypropylene	x				
	Polyolefin	x				
<b>4. Crumb rubber</b>	Different sizes, treatments, and processes	x	x	x		
<b>5. Oxidants</b>	Manganese compounds	x				
<b>6. Hydrocarbons</b>	Aromatics			x		
	Napthenics					
	Paraffinics/wax				x	
	Vacuum gas oil			x		
	ROSE process resins	x				
	Asphaltenes	x				
	Tall oil	x	x			
	Natural asphalts	x				
<b>7. Antistrips</b>	Fatty amidoamines					x
	Imidazolines					x
	Polyamines					x
	Hydrated lime					x
	Organo-metallics					x
	Acids					x
<b>8. Fibers</b>	Polypropylene	x	x	x		
	Polyester	x		x		
	Cellulose	x				
	Mineral	x				
	Reinforcement	x	x	x		
<b>9. Antioxidants</b>	Carbamates					
	Lead			x		x
	Zinc			x		x
	Carbon black	x				x
	Hydrated lime				x	x
	Phenols					x
	Ethyoxylated amine				x	x

1: PD: Permanent Deformation

3. LTC: Low Temperature Cracking

2. FC: Fatigue Cracking

4. MD: Moisture Damage

5. AGN: Oxidative Aging

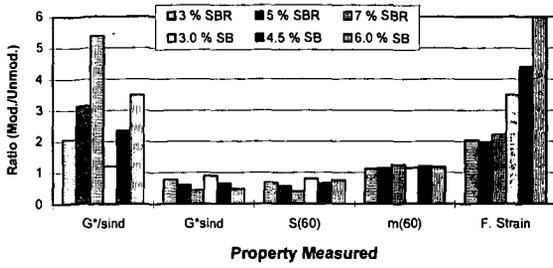


Figure 1. Relative Change in Superpave binder properties after modification with SBR and SB-based modifiers

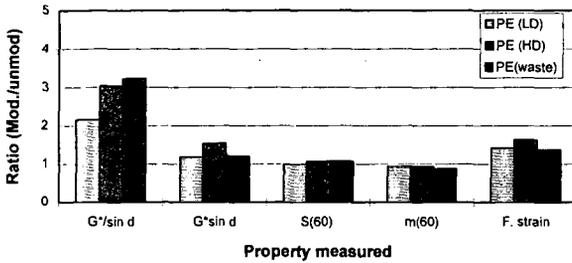


Figure 2. Relative Change in Superpave binder properties after addition of Plastomers

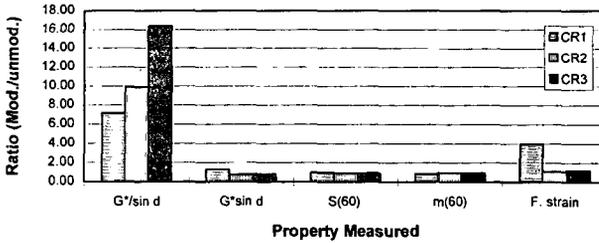


Figure 3. Relative change in Superpave binder properties after modification with 3 types of crumb rubber

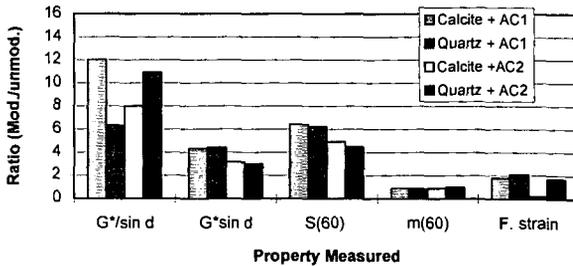


Figure 4. Relative change in Superpave binder properties after addition of mineral fillers

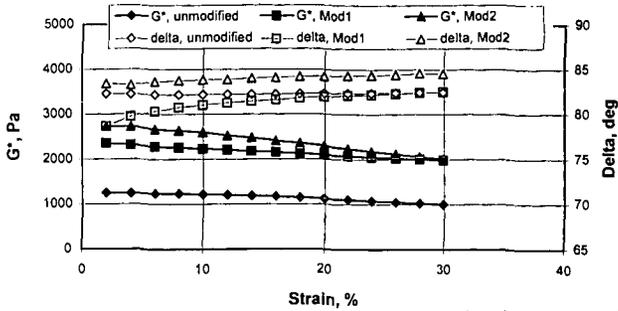


Figure 5. Effect of testing strain on properties of a typical asphalt before and after modification with polymers

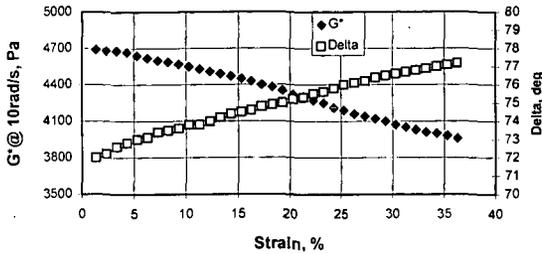


Figure 6. Effect of testing strain on properties of a typical asphalt modified with crumb rubber

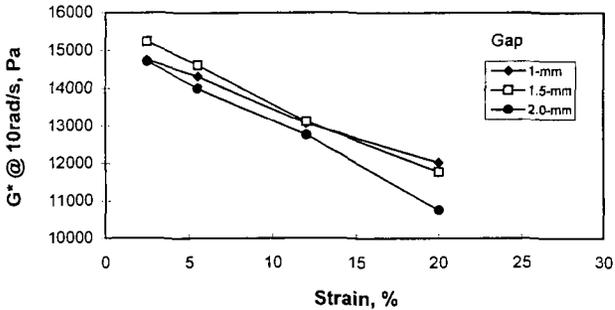


Figure 7. Strain dependency of asphalt filled with rigid filler (Ottawa sand < 0.25 mm) Filler/Asphalt ratio= 0.5 by volume

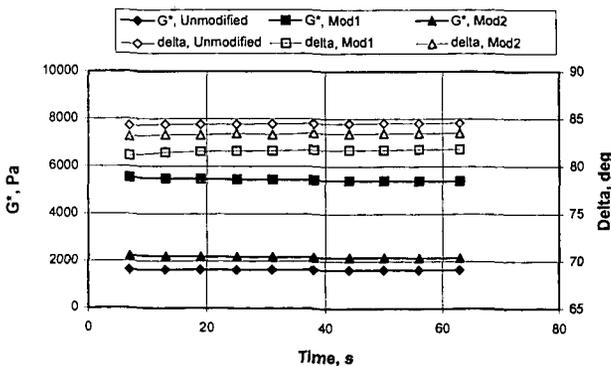


Figure 8. Effect of mechanical working on asphalt properties before and after modification with polymers