That Old Black Magic... Modernized and Demystified

BY TIM BARRETT, RRC, CDT

Diagrammatic SEBS illustration, courtesy of Shell Chemical.

S
tyrene-Ethylene-Butylene-Styrene polymer-modified mopping bitumen (SEBS•PMB) has emerged from the shadows of the specialty marketers and is now offered by many mainstream BUR and modified bitumen manufacturers. At last count, 21 different manufacturers were marketing or making available SEBS polymer-modified mopping asphalt as a part of their warranted roof systems.

Some of the manufacturers offer multiple grades of SEBS polymer-modified asphalt so the actual number of different SEBS polymer-modified bitumen choices exceeds 50. The marketing and technical information available from the manufacturers for the wide array of SEBS•PMB choices presents a variety of claims and conflicting information for the roofing professional to sort through.

The ASTM D-8.03 subcommittee recognized the market confusion surrounding SEBS•PMB and sought to clarify the indiscriminate claims and market disorder by developing a standard for SEBS•PMB. From ASTM’s unique consensus-forming committee work, ASTM D 6152, “Standard Specification for SEBS—Modified Mopping Asphalt Used in Roofing” was approved in late 1997. It is significant to note that the ASTM scope states that, “1.3, the specified tests and property values used to characterize SEBS•PMB modified asphalt are intended to establish minimum properties” (italics are those of author).

The ASTM standard sets forth nine criteria with minimum, and where applicable, maximum ranges for SEBS•PMB properties (as shown in the table on page 8). The properties are to be measured “as manufactured” unless otherwise noted. Properties the ASTM standard addresses are:

1. Softening point, (ASTM D-36)

This test procedure measures the temperature at which a metal ball falls a given distance through a shouldered disk filled with the tested asphalt (ring and ball). The result provides an approximation of the transition temperature between a viscous solid and a thick flowable liquid, the approximate melting temperature. The higher the softening point temperature, the more resistant the material is to flow at elevated roof temperatures.
2. Softening point change after heat exposure (ASTM D-36)

This test follows the same protocol as D-36 softening point test after the SEBS asphalt is heated to 500°F for 8 hours. The ability of the material to retain softening point gives a good indication of the ability of the SEBS•PMB to remain stable and resist thermal degradation at typical application temperatures.

3. Flash point (ASTM D-92)

Flash point measures the temperature at which fumes above the asphalt will ignite if exposed to an external ignition source. Higher flash points indicate lower flammable volatile content. High flash also indicates the material can be heated to hotter temperatures with less risk of fire in the kettle. This measure is generally considered as a safety issue and not a performance issue. This standard requires a minimum flash point of 500°F. ASTM D-312 asphalts have a minimum flash point of 475°F.

4. Penetration: before heat exposure (ASTM D-5)

Penetration measures the depth that a standard needle weighing 100 grams penetrates a material at 77°F in five seconds. The result provides an indication of the stiffness of a material at the test temperature. A softer, SEBS polymerized asphalt (more rubber-like than asphalt-like) will allow for greater penetration than conventional asphalt. Penetration at 77°F does not provide much indication of performance at hot or cold temperatures.

5. Penetration after heat exposure (ASTM D-5)

Following the same test procedures as penetration before heat exposure, penetration is measured after the SEBS•PMB has been exposed to 500°F heat for 8 hours. After heat exposure, most asphalts will become stiffer with less penetration. If a modifier is used which breaks down during heat exposure, the penetration will tend to increase significantly. The ASTM D-6152 standard allows a maximum of 12 units change, plus or minus, after heat exposure.
6. Solubility in trichloroethylene, % (ASTM D-2024)

This test requires 99% solubility which shows that virtually all of the SEBS•PMB components are soluble, and the material does not contain more than 1% undesirable additives or residues such as mineral filler, fibers, lime, clay, or refinery impurities.

7. Tensile-Elongation, % at 77°F, (ASTM D-412)

Tensile indicates the breaking or ultimate strength of a material. To compare materials, test conditions need to be the same. The tensile strength will vary depending on temperature, load rate, and specimen configuration. Higher tensile strengths indicate a higher strength and greater resistance before breaking. Tensile strength can be measured using a variety of procedures including ASTM D-412.

Elongation (the flip side of the stress-strain equation) measures the amount of extension (in percent) that a material will permit before breaking. Results will vary depending on temperature, loading rate, and configuration. The test is somewhat similar to ductility (with ductility testing, each three cm is equivalent to approximately 100% elongation). Higher elongations indicate greater stretching ability prior to breaking. The ASTM D-6152 standard requires a minimum of 750% elongation at 77°F. Type III asphalts typically have elongations of 80% or more at 77°F and 0% elongation at +20°F. Polymer-modified materials typically have high elongation properties across a wide temperature span. High quality SEBS•PMB can have over 1000% elongation at both 77°F and 0°F.

8. Recovery (ASTM D-412)

Recovery measures the ability of a material to return to its original dimensions after being extended. Test procedures can vary significantly. Higher recovery indicates increased elasticity. The test method specifies temperatures, extension rate and amount, and the recovery time period. This property test helps distinguish elastomeric material from non-elastomeric, low-modulus material. After 300% extension at 73°F, a minimum recovery of 80 percent is required. Polymer-modified materials experience substantially more elastic recovery than air-blown roofing asphalt.

9. Cold Bend (ASTM D-3111)

Cold Bend standard procedures can vary somewhat in exact methodology. This test procedure generally consists of casting a specimen (0.079 inch in thickness), conditioning at the test temperatures for 24 hours, and then bending the specimen around a mandrel (1 inch diameter) a specific amount (typically 90°) at a uniform rate in a specified period (usually 2, 5, and 10 seconds). A passing result is one in which the specimen does not crack. This test provides an indication of low-temperature flexibility characteristics of a material. Passing results at lower temperatures indicate better low temperature fracture resistance from impact, expansion, and contraction forces. Type III asphalt will typically have a fracture temperature (measured using a 1 inch diameter mandrel and a 90° bend in 10 seconds) of +35°F to +70°F, depending upon the quality and nature of the asphalt. SEBS•PMB ranges from -30°F to +20°F or higher for different grades of material. The ASTM D-6152 standard requires a minimum low temperature flexibility of +20°F.

10. Ductility (ASTM D-113)

Ductility measures the distance in centimeters that a material can extend at 77°F at a rate of 5 centimeters per minute. The ASTM D-312 Type III asphalt specification requires a minimum of 2.5 cm extension, and Type IV asphalt requires a minimum of 1.5 cm extension. The longer the ductility, the greater the extension a material can take before fracture at that temperature. Ductility of polymer-modified roofing asphalts typically ranges from 25 to 70 cm. Ductility is not a requirement of ASTM D-6152; however, it is required by the ASTM D-312 asphalt standard and is noted for comparative reference.

HISTORY

SEBS polymer was developed by Shell Chemical as a “second generation” of the Styrene-Butadiene-Styrene (SBS) type polymer. Through a manufacturing process called hydrogenation, SBS polymer undergoes a chemical transformation, developing into SEBS. In very simple terms, the Ethylene “E” molecule adds significant thermal stability and ultraviolet resistance to the SBS polymer. SEBS polymers have been widely used in the adhesives industry and the automotive manufacturing industry for more than two decades. SEBS is the adhesive that holds “Topside” boating shoes together during constant wetting and drying cycles. Gerber uses it for knife handles. There are literally thousands of unique and demanding applications utilizing SEBS polymer.

SEBS•PMB was first sold in the U.S. roofing industry as a mopping bitumen by two competing companies in the early 1980s. Both of those suppliers generally had very high quality product which significantly exceeded the minimum property requirements set forth in the current ASTM D-6152 standard.

By the mid-1980s, there were five companies marketing SEBS•PMB in the specialty roof market at the relatively high prices of $1,400 to $2,300 per ton compared with about $200 per ton for Type III asphalt.

By the early 1990s, after 10 years of in-place field performance, high quality SEBS•PMB had clearly proven itself as an engineered enhancement of BUR and mod-bit roofing systems. The beneficial enhancements provided by SEBS•PMB were generally recognized within the industry by this point in time. Some of the “major” manufacturers took notice of the “specialty” marketers’ success with SEB•PMB and started to compete with the “specialty” manufacturers, offering their own SEBS•PMB-based systems.

By the mid 1990s, there were a dozen roofing material manufacturers, both “major” and “specialty” purveyors, offering SEBS bitumen as a component of their warranted assemblies.

Polymerization

As the popularity and market share of SEBS bitumen has increased, so has competition among the various manufacturers. In classic form, this competition has tended to drive prices
down. The competition also motivated the implementation of "value-engineering" principles to the formulations used to produce the SEBS•PMB products. "If it ain't broke, fix it until it is" mentality has been used by some SEBS•PMB value engineers, according to one noted expert in the field. SEBS polymer is relatively expensive with costs of about $2.50 per pound compared with an SBS cost of about $.70 per pound. One manufacturer tried replacing part of the SEBS polymer content with crumb rubber from reclaimed tires with poor results. Some manufacturers tried replacing part of the SEBS polymer with the less expensive SBR, SBS or SIS polymers with poor results, and some started using filler in the product.

A common response to the increased competition and price erosion was for manufacturers to reduce their costs by simply decreasing the amount of SEBS polymer used in the formulation of the material. All other things being equal, this generally will result in a corresponding decrease in product quality, particularly in the areas of elastomeric properties, cold temperature flexibility, and strength. Perhaps to fight this trend, certain bid specifications sometimes require a prescribed percentage of SEBS polymer. Unfortunately, one cannot judge SEBS•PMB solely on the claimed percentages of SEBS polymer content.

SEBS•PMB must ultimately be judged by the mechanical and rheological properties of the finished product relative to the properties desired and the properties published. The ASTM D-6152 standard sets the protocol and minimum benchmarks to accomplish that judgment.

The quality determinants of SEBS•PMB are:

• Polymer type selection.
• Quality and quantity of polymer loading.
• Quality and consistency of base asphalt.
• Quality of the mixing process.

"SEBS" is not a specific product but rather a broad class of polymers which vary in molecular architecture. They are "designed" for many different applications in addition to asphalt modification. SEBS polymer can be linear or radial, low molecular or high molecular weight. Its proportion of styrene to ethylene-butylene can vary, and its viscosity can vary, among other possible variations which affect the end product.

In addition to the type and percentage of SEBS polymer content, the quality of SEBS•PMB will be highly influenced by the compatibility factor of the base asphalt. The polymers are mixed with the base asphalt using either a high or low shear mixer with the appropriate manufacturing techniques. Low shear and high shear manufacturing processes each produce different results, although satisfactory results can be obtained from either.

**Base Asphalt**

Asphalt bitumen is the residue of certain crude oils after removal of most volatile components, typically by a distillation process. Crude oil quality is of the first order of importance in determining the characteristics of the asphalt from which it is produced. Crude oil composition is not uniform, and it may be stated that there exist as many kinds of crude oil as there are oil fields in the world. Each is as unique and individual as a finger-print. Depending on the constituents of the individual crude oil, the asphalts obtained from them will contain various hydrocarbons and hydrocarbon groups in different proportions.

At the turn of the century, asphalt was considered a waste byproduct of the crude oil distillation process, much the same as coal tar pitch was the detritus of coal-fired energy production. Crude oil can have asphaltic content that ranges from nil to as much as 70%. Much asphaltic-rich crude oil is used as fuel oil. Current U.S. production of asphalt is 60 million tons, which is produced by less than 50 primary asphalt refineries.

The more important constituent groups in asphalt can be determined by simple testing. They include:

• Carboids which are insoluble in carbon disulfide.
• Carbenes which are insoluble in carbon tetrachloride and soluble in carbon disulfide.
• Asphaltines which are insoluble in low boiling saturated hydrocarbons and soluble in carbon tetrachloride.
• Malthenes which are soluble in low boiling saturated hydrocarbons.

The carboid and carbene components of commercial asphalts are slight and increase only during cracking. Base asphalt quality is largely determined by the quantity and nature of the asphaltene and malthene components.

The hard, rigid asphaltenes in asphalt are con-
sidered incompatible with the polystyrene domains in SEBS polymer. As a general guide, if the asphaltene content is over ten percent by weight, the asphalt will probably be incompatible with SEBS polymerization. A higher than usual amount of aromatics in the asphalt can soften the polystyrene domains in the polymer and make the asphalt more compatible, but it will also lower the ultimate tensile strength of the SEBS•PMB.

Asphalt characteristics will differ when the asphalt is manufactured from the same crude by different manufacturing methods, or with different crudes which are processed by the same manufacturing method. The most common processes for asphalt manufacture are distillation and extraction. Blowing of asphalt is considered further modification of asphalt in the manufacturing process.

Asphalt produced by distillation is called “straight run” asphalt or asphalt “flux.” It is commonly used to manufacture paving grades of asphalt cement, such as AC 10 and AC 20. Straight run asphalt can be distinguished from “blown” asphalt by a number of physical properties. Blown roofing asphalt is asphalt flux which has been “oxidized” with a heat and steam process to elevate the softening point to conventional ASTM D-312 roofing asphalt specifications. Unmodified roofing asphalts usually are “blends” of several different asphalts which have high asphaltene content by design.

Most modified bitumens, both SBS and SEBS, are made with straight-run asphalt. Oxidized asphalt has not proven suitable to most manufacturers for producing polymer-modified asphalts. Phase separation between the polymer and asphalt has been a common problem when blown asphalt is used to make SEBS•PMB.

It is also commonly accepted that using straight-run asphalt that has not been oxidized will result in slower aging and greater longevity of the SEBS•PMB as compared with air-blown asphalt. The oxidizing process of asphalt is an accelerated aging of the asphalt which raises its softening point and flow resistance to a temperature where it can be used on a roof without slippage or displacement. After asphalt is applied on roofs, its softening point will continue to rise as it ages and becomes increasingly brittle.

### Market Development

As the competitive battles of the SEBS•PMB manufacturers continued in the ’90s, some manufacturers continued to reduce polymer content to a point where some asphalts marketed as “SEBS polymer-modified asphalt” had such small amounts of polymer it was insufficient to form a polymer network, the primary objective of polymerization (see illustration, page 6). Some field samples tested by the author have such minuscule polymer loading, they actually had to have the polymer measured in parts per million.

Some otherwise reputable manufacturers are currently promoting SEBS bitumen in their product offering that is manufactured with only one to two percent polymer loading and nominally holding them out as the equals to high grade SEBS polymer-modified bitumen. Two percent polymer loading is insufficient polymer to form a polymer network with even the best base asphalt. With present technology, two percent polymer loading is insufficient polymer to form a polymer network with even the best base asphalt. With present technology, two percent polymer

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<thead>
<tr>
<th>ASTM D-6152</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F-1</th>
<th>F-2</th>
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1Values as manufactured. 2Properties are not part of ASTM D-6152. Columns A-K represent individual manufacturers. Numbers represent different grades from the same manufacturers. Information extracted from manufacturers’ published literature. Blank spaces are unpublished information.

There is a minority view within the industry which claims that SEBS•PMB can be successfully manufactured with blown asphalt by changing certain mixing procedures and adding carbon black compounds. However, many believe the resultant product will not provide the extended longevity of unoxidized, “straight-run” asphalt, and it is doubtful that such a material would pass the solubility requirements of ASTM D-6152.

When all of the variables of asphalt are evaluated and considered, it is generally thought that about 80 percent of all asphalt is incompatible with SEBS polymerization, 12 percent somewhat compatible, and 8 percent ranging between compatible and very compatible.

The use of a higher percentage SEBS polymer content with “somewhat compatible” asphalt can result in a product of lower quality than a SEBS•PMB made with less polymer and a “very compatible” base asphalt. The relationship between asphalt compatibility and polymer loading is intertwined inseparably. Proper formulation is a balancing act with the objective of blending the components to be and remain “in phase” with each other for the service life of the roof.
loading is insufficient to meet ASTM D-6152 standards.

In many cases, the price of the low-grade SEBS•PMB product is commensurate with the quality of the product, which is to say it is not very expensive and there is some beneficial improvement in the asphalt, albeit slight. Some contractors, motivated by economics, will find this type product to be an attractive option and can be expected to aggressively promote the product in competition with higher quality and higher priced SEBS•PMB. If such contractors are successful, it will be at the expense of the building owner and to the detriment of system performance.

In a few cases, the price of a low polymer content product is very high relative to the quality of the product, creating a classic caveat emptor situation. Sales and marketing obfuscation will almost always accompany this type product. This can be quite misleading to the unassuming or uninformed.

In a related development, the NJ State Commission of Investigation (SCI) held public hearings on December 8 and 15, 1999. The SCI alleged that a roofing material manufacturer and its contractors substituted “cheaper” materials for those specified on certain school reroof projects, defrauding the school boards of more than $10 million dollars. Some of the substitutions involved SEBS-based materials. (Editor’s note. See article, page 40).

Conclusions

High quality SEBS•PMB has stood the test of two decades of field experience and clearly provides an opportunity to improve the performance and presumably the longevity of BUR and mop-applied SBS mod-bit systems.

SEBS•PMB is offered by many manufacturers in many grades in a wide spectrum of prices.

The experiential history of SEBS•PMB was forged with relatively high quality material from the various pioneers of the industry. Some newer, less polymerized formulas are marketed and promoted by some manufacturers as though they are the same product as the higher polymerized product which developed the successful track record. They are not the same.

The roofing system performance enhancements provided by SEBS•PMB, meeting or exceeding ASTM D-6152 standards, are worthy of consideration by specifiers, consultants, and owners who desire roofing systems with performance characteristics which are demonstrably greater than those of conventional ASTM D-312 asphalt based systems.

The performance enhancements provided by SEBS•PMB which does not reach the minimal levels of ASTM D-6152 standards will not provide significant enhancement to the roof system performance. Such products should not be confused with the proven performance record established by high quality SEBS•PMB.

If low performance, low polymer content SEBS•PMB is purchased at a corresponding low price, the nominal improvement of system performance may be worth evaluating by a seasoned roofing professional.

Recommendations

ASTM has published minimum standards of performance for SEBS•PMB which approximate a basic minimum level of asphalt polymerization or a “network” structure. Specifiers and users can and should use the ASTM standard as a guide to:

- Accept ASTM minimum standards for SEBS•PMB for significant performance increases.
- Accept less than ASTM minimal standards for SEBS•PMB at a lower cost for nominal performance improvement.
- Require SEBS•PMB standards of performance higher than ASTM standards, as is encouraged and promoted by some manufacturers, for substantial performance increases.

As is usual for our industry, an intelligent and informed roofing professional should be able to sort through available information, ask the right questions, examine the evidence, and ultimately choose wisely.

References and Further Study:

ASTM, Section 4, Construction, Vol. 04.04 Roofing, Waterproofing and Bituminous Materials.


Shell Chemical literature.

Various manufacturers’ literature.


About the Author

Tim Barrett, is President of the Barrett Company, Millington, NJ (www.barrettroofs.com) and has been involved with the manufacture, sales, and installation of polymer modified asphalts since 1975. Tim is a Registered Roof Consultant and an active member of the Continuing Education Committee of the Roof Consultants Institute.