# POLYMER MODIFIED ASPHALT

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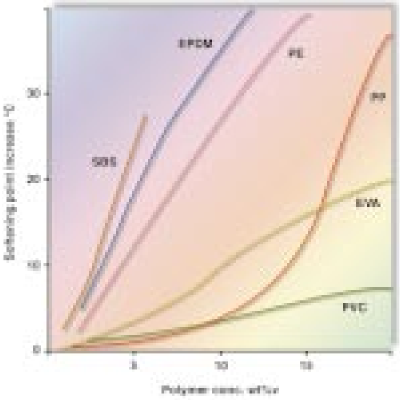

*Considering the international position of Venezuelan oil industry as one of the leaders of the current world asphalt production, it is important to be aware of the source of opportunities that polymer modified asphalt (PMA) offers in today's market. Based on that, this paper presents an overview of the characteristics of polymer-asphalt binders, mostly used in the paving industry. Emphasis is being made on the relationships of composition and formulation with the properties of the binder, and the relationships of the binder properties and performance of the mixture. Although polymer modification seems to be the best solution to improve asphalt properties, these systems present three main problems: a) poor asphalt polymer compatibility (which influences the stability of the system), b) higher viscosities during asphalt processing and application, and c) higher cost. These issues are also covered in the present study, altogether with some field experiences. A summary of advantages and disadvantages of most used polymers to modify asphalt binders (styrene-butadiene-styrene (SBS), reclaimed tire rubber, polyethylene (PE), and atactic polypropylene (aPP)) is also provided.*

*Considerando el posicionamiento internacional que tiene la industria petrolera venezolana como uno de los líderes en la producción actual de asfaltos a nivel mundial, es importante conocer la fuente de oportunidades que ofrecen los asfaltos modificados con polímeros (PMA del inglés "polymer modified asphalts") en el mercado actual. Con base en ello, se presenta en este estudio una visión de las características de los asfaltos con polímero, usados mayormente en la industria de la pavimentación. Se hace énfasis en las relaciones de la composición y formulación con las propiedades del ligante y las relaciones de las propiedades del aglutinante y el comportamiento de la mezcla. Aun cuando la modificación con polímeros parece ser la mejor solución para mejorar las propiedades del asfalto, estos sistemas presentan tres inconvenientes principales, a saber: a) poca compatibilidad asfalto-polímero (lo cual afecta la estabilidad del sistema), b) viscosidades elevadas durante el procesamiento y aplicación del asfalto y c) altos costos. Estos aspectos también son analizados en este trabajo, indicando algunas experiencias de campo. Se incluye, además, un resumen de las ventajas y desventajas de los polímeros más usados para modificar asfaltos (estireno-butadieno-estireno (SBS del inglés "styrene-butadiene-styrene"), caucho recuperado, polietileno (PE), y polipropileno atáctico (aPP)).*

Some improvements in asphalt properties have been achieved by selecting the proper starting crude, or tailoring the refinery processes used to make asphalt. Unfortunately, there are only a few crudes that can produce very good asphalts, and only a limited number of actions that can be taken to control the refining process to make improved asphalts.

The next step taken by the industry was to modify the asphalt. Air blowing makes asphalt harder. Fluxing agents or diluent oils are some times used to soften the asphalt. Another method that can significantly improve asphalt quality is the addition of polymers. This review will mainly deal with the asphalts for road construction, since approximately 85% of the asphalt goes to the pavement industry. The term "polymer" simply refers to very large molecules made by chemically reacting many small molecules (monomers) to produce long chains. The physical properties of a specific polymer are determined by the sequence and chemical structure of the monomers from which it is made, its molecular weight and molecular weight distribution. When polymers are added to asphalt, the properties of the modified asphalt cement depend on various things:

- Polymer characteristics
- Asphalt characteristics
- Mixing conditions
- Compatibility of polymer with asphalt.

Improvement in rutting resistance, thermal cracking, fatigue damage, stripping, and temperature susceptibility have led polymer modified binders to be a substitute for asphalt in many paving and maintenance applications, including hot mix, cold mix, chip seals, hot and cold crackfilling, patching, recycling, and slurry seal. They are used wherever extra performance and durability are desired. In many cases, they are selected to reduce life cycle costs. Polymer modified binders have allowed the use of paving techniques previously not viable, such as micro-surfacing and use of emulsion chip seals on high traffic roads. Specifiers are finding that many of the Superpave binder grades (Superpave: SUperior PERformance PAVEment), the final product of the Strategic Research Highway Program (SRHP), 1987-1992), need polymer modification to concurrently meet the requirements for high temperature rutting resistance and thermal cracking resistance at low temperature.

The United States, China, France and Italy are leaders in polymer modified asphalt (PMA) research and development activities, even though considerable work has also been done in Japan, Germany, Russia, Great Britain, and Canada.

## GENERAL

The main reasons to modify asphalts with polymers could be summarized as follows [1]:

- To obtain softer blends at low service temperatures and reduce cracking
- To reach stiffer blends at high temperatures and reduce rutting
- To reduce viscosity at layout temperatures
- To increase the stability and the strength of mixtures
- To improve the abrasion resistance of blends
- To improve fatigue resistance of blends
- To improve oxidation and aging resistance
- To reduce structural thickness of pavements
- To reduce life costs of pavements.

The rheological behavior of asphalt-polymer blends is of great interest because it is closely related to the performance of pavements. Furthermore, the addition of small amounts of polymer dramatically changes the rheological properties of the asphalt. The addition of polymer introduces an additional difficulty to the asphalt complexity, because of its high molecular weight. The formation of a homogeneous system is not easy and incompatibility problems arise.

Since a modified binder consists of two distinct phases, three different cases must be considered for modified systems [2]:

### Low polymer content

In this case, the bitumen is the continuous phase of the system, and the polymer phase (less than 4%) is dispersed through it. Due to its lowered oil content, the bitumen phase has a correlatively higher asphaltene proportion. As a result, both the cohesion and elasticity of the asphalt are enhanced. In addition, the polymer phase is dispersed through the bitumen matrix. At high service temperatures (around 60°C), the stiffness modulus of the polymer phase is higher than that of the matrix. These reinforcing properties of the polymer phase improve the mechanical performance of the binder. At low temperatures, the stiffness modulus of the dispersed phase is lower than that of the matrix, and reduces its brittleness. Briefly, the dispersed polymer phase enhances the properties of the binder both at low and at high service temperatures. In other words, the polymer extends the useful temperature range for the asphalt. In this case, the choice of bitumen is a determining factor. These materials are usually employed for paving.

### Polymer content around 5%

This system may show microstructures in which the two phases are continuous and interlocked. Such systems are generally difficult to control and pose stability problems (their micromorphology and properties often depend on temperature history).

### Sufficiently high polymer content

More than 7% in general, if the bitumen and polymer are correctly chosen. The polymer phase is the matrix of the system. This is in fact not a bitumen, but a polymer plastified by the oils in the bitumen in which the heavier fractions of the initial asphalt cement are dispersed. In this case, the polymer is the continuous phase and the asphalt is therein dispersed. The properties of such a system are fundamentally different to those of a bitumen, and depend essentially on those of the polymer. One should speak not of a polymer modified bitumen, but of a thermoplastic adhesive. These materials are usually employed for roofing.

Over the last two years, USA is the country where most of the research is done, followed by China, Canada and some European countries (France, Italy, Great Britain and Spain). Among the companies that have been filing patents on PMA over the last two years, Marathon Ashland Petroleum LLC is the leading one. The Goodyear Tire & Rubber Company, Fina Technology, Polyphalt LLC, BASF Corporation and Ergon Incorporated are also reported.

There have been lots of movements in the marketing area. The interest for PMA technology has been increasing, and so the number of companies which commercialize it, and their earnings. For example, Canada based Polyphalt, which develops and markets polymer modified asphalt reports its revenues (from royalties and license fees) increased 119 percent in the nine-month period ended on December 31, 2001 [3]. New PMA plants have also been opened.

In the most recent study (February, 2000) from the Freedonia Group on Asphalt Products and Markets US demands for asphalt products is forecasted to advance three percent per annun through 2003, and so will do the adoption of the Superpave program's performance based specifications for road projects. This will generate a greater demand for polymer modified asphalts [4].

## POLYMERIC ADDITIVES

Many polymers have been used as binder modifiers, and they can be classified into five groups:

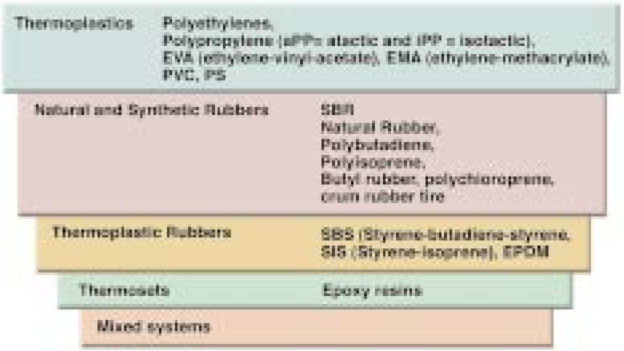

Table 1 shows a summary of these polymers and their advantages and disadvantages as asphalt modifiers.

As it was shown, many different polymers are used to modify asphalts and each has their own associated physical properties. For example, ethyl vinyl acetate (EVA) stiffens the asphalt, much like a hard plastic, so it is considered a plastomer. Styrene butadiene (SB) and styrene butadiene styrene (SBS) block copolymers can increase the elasticity of the asphalt, much like a rubber band, so they are considered elastomers. Another group of elastomeric polymers, styrene butadiene rubber (SBR) latex polymers, increases the ductility of asphalt cements. Fig. 1 shows how the softening point of specific asphalt changes with different polymers at different concentrations.

Today, SBS, despite its low aging resistance, is probably the most appropriate polymer for asphalt modification [14]. Nevertheless, some authors claim that the addition of SBS type block copolymers has not only economic limits, but it

**Table 1. Characteristics of polymers used to modify asphalts [5-13].**

| Polymer | Advantages | Disadvantages | Uses |
|---|---|---|---|
| Polyethylene (PE) | High temperature resistance<br>Aging resistance<br>High modulus<br>Low cost | Hard to disperse in the bitumen<br>Instability problems<br>High polymer contents are required to achieve better properties.<br>No elastic recovery | Industrial uses<br>Few road applications |
| Polypropylene (PP) | No important viscosity increase<br>even though high amounts of polymer are necessary (ease of handling and layout)<br>High R&B<br>Low penetration<br>Widens the plasticity range and improves the binder's load resistance | Separation problems<br>No improvement in elasticity or mechanical properties<br>Low thermal fatigue cracking resistance. | Atactic PP is used for roofing<br>Isotactic PP is not commercially applied |
| Ethylene-vinyl-acetate (EVA)<br>Ethylene-methacrylate (EMA) | Outstanding compatibility in some cases.<br>Minimal viscosity changes compared to competitive products.<br>Thermally stable at normal mixing and handling temperatures.<br>Low cost, as compared to block copolymers<br>Increased tack. | No improvement in elastic recovery | Paving and roofing |
| PVC | Lower cracking PVC disposal | Acts mostly as filler | Not commercially applied. |
| Styrene-butadiene block copolymer (SBS)<br>Styrene-isoprene block copolymer (SIS) | Higher flexibility at low temperatures (*)<br>Better flow and deformation resistance at high temperatures<br>Strength and very good elasticity<br>Increase in rutting resistance | High cost<br>Reduced penetration resistance<br>Higher viscosity at layout temperatures<br>Resistance to heat and to oxidation is lower than that of polyolefins (due to the presence of double bonds in the main chain) | Paving and roofing |

(*) Some authors may disagree.

**Table 1. (Cont.).**

| Polymer | Advantages | Disadvantages | Uses |
|---|---|---|---|
| | Higher aging resistance<br>Better asphalt-aggregate adhesivity<br>Good blend stability, when used in low proportion. | Asphalts suitable for SBS blends, need an asphalt with a high aromatic and a low asphaltene content. | |
| EPDM | Higher dispersion capacity (due to their lateral olefinic groups, with double bonds and great volume) and improved elastic behavior as compared to PE.<br>High proportions needed in order to appreciate an performance improvement. | Miscibility with the asphalt is not easy<br>Sometimes air blowing is necessary to produce less unstable PMA (through formation of some crosslinking). | Roofing |
| Epoxy resins | They don't exhibit viscous flow<br>Very resistant to chemical attack<br>Less temperature susceptible<br>Higher flexibility<br>Cracking resistance<br>Better adhesivity. | High cost<br>Blended with asphalts, the binders display the behavior of thermosetting resins rather than those of asphalts. | Used in a variety of special applications such as a airport paving and bridge surfacing. |
| Natural rubber | Better rutting resistance<br>Higher ductility<br>Higher elasticity and properties under cyclical loads. | Sensitive to decomposition and oxygen absorption.<br>Too high molecular weight (low compatibility). Therefore, it must be partially decomposed and mechanically homogenized. | Paving |
| Polydiolefins (polybutadiene, polyisoprene) | Easier to disperse than polymonoolefins.<br>They confer characteristics of elasticity more evident than other thermoplastic materials. | The double bonds in all chains can lead to a partial decomposition of the polymer chain by heating or in the presence of oxygen. | Paving<br>Roofing |
| Reclaimed tire rubber | Rubber disposal<br>Low material cost<br>Potential fatigue resistance improvement<br>Reduced reflective cracking<br>Longer durability using thinner lifts<br>Lower rutting resistance. | Lower physical resistance if used as an extender.<br>Use of proprietary products.<br>It needs high T and long digestion times in order to be dispersed in the bitumen. If not partially devulcanized, it produces a heterogeneous binder with the rubber acting mainly as a flexible filler | Paving |
| Mixed systems (most used systems include SBS in their formulation (Systems with PE have been also used). | Improvements that may not be possible with a single modifier. | Compatibility and instability problems | Paving |

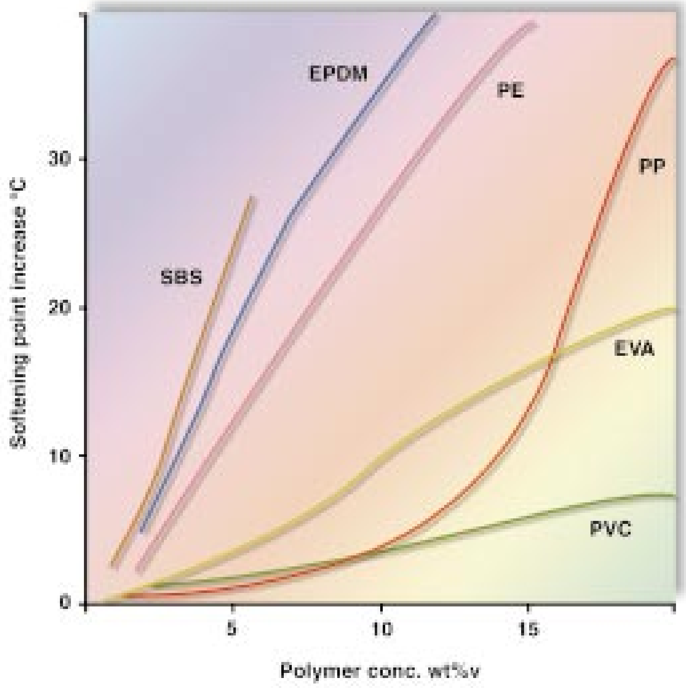

*Fig. 1. Typical correlations between the softening point of some polymers used as modifiers and their concentration in the asphalt blend [7].*

shows serious technical limitations: despite an increase in the low temperature flexibility, a decrease in strength and resistance to penetration is observed, particularly at higher temperatures.

Most polymers described until now are physically dispersed into the asphalt, but do not chemically react with it. These polymers can be functionalized to produce a polymer additive that can chemically react with the asphalt matrix. Commonly, a thermoplastic copolymer is blended with a chemical compound, *e.g.* fatty dialkyl amide, ending with a functional group that will react with the asphalt. Examples of some functionalized polymers used to modify asphalt are SEBS-g-MAH, Zn-sulfonated-SBS.

Over the last two years, the major concern in the literature has been towards improving the stability and compatibility of the asphalt-polymer blends optimizing the blend formulation. Rheological studies of these systems are also common.

An increasing tendency of using sulfur in asphalt and polymer modified asphalts, was observed. The sulfur has been incorporated in different ways:

- In the neat asphalt prior blending with polymer
- In the polymer prior blending with asphalt
- In asphalt-polymer blends
- As a slurry of solid sulfur in oil.

Polymer-asphalt blends prepared with the sulfur cogglomerated polymers show improved storage stability. Also, when using the sulfur slurry, polymer use is optimized because the polymer matrix development can be completed before cross-linking occurs [15].

Also, an increasing interest on incorporating two or more different polymeric materials in bitumen such as polyethylene and SBS was observed. The ability to incorporate different polymers in asphalt allows desirable modifications to the properties of the composition to be affected [16].

The use of mineral acids in the asphalt-polymer compositions was described in a few studies. The addition of mineral acid to the system widens the temperature range in which satisfactory performance from a given polymer asphalt composition can be achieved, hence reduces the amount of polymer additive that would otherwise be needed [17].

## HOW POLYMERS ARE INCORPORATED INTO ASPHALT

Two methods are commonly used to incorporate polymers into asphalt:

- Addition of latex polymer to the asphalt. This method is relatively easy and trouble free.
- Addition of solid polymers to asphalt. This method normally requires substantial mixing and shearing in order to uniformly dispersed the polymers, particularly when SBS or SIS block copolymers are used.

At room temperature, SBS materials show similar behavior to that of a crosslinked network, because the polystyrene (PS) end blocks aggregate into rigid domains, whereas the polybutadiene (PB) or polyisoprene (PI) blocks act as elastic amorphous unions between them (Fig. 2).

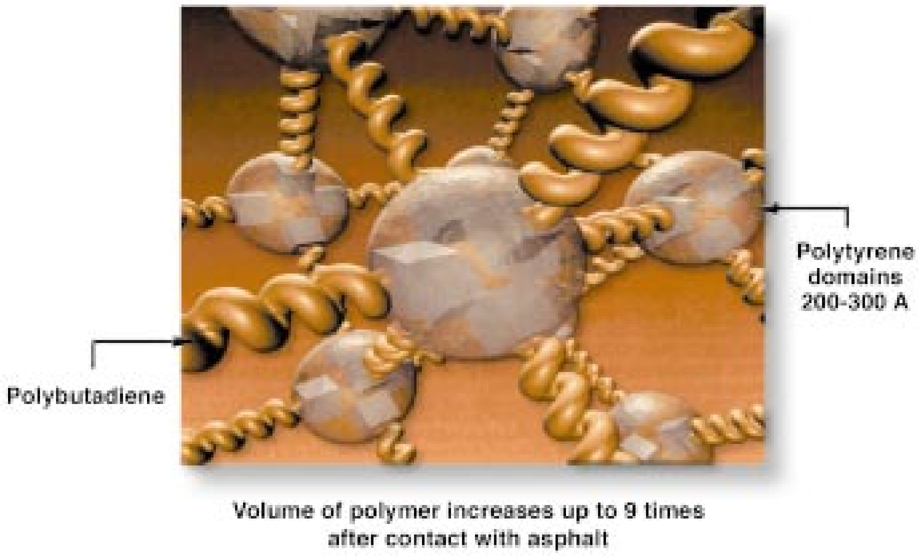

*Fig. 2. Scheme of SBS molecules blended with asphalt [5].*

Because their "tridimensional" network is only physical, unlike other crosslinked materials, they become fluid at high temperatures, thus facilitating their mixing and processing.

When adding a functionalized polymer to asphalt, specific interactions between asphalt and the polymers, such as hydrogen bonding can take place. Also, some chemical reactions could take place between the functional groups of the components of the blends. When functionalized polymers are blended, reactive or chemical compatibilization can occur, giving rise to the formation of *in-situ* copolymers due to the chemical reaction during processing [16].

A good example, of a polymer that reacts with asphalt, is the product commercialized by Dupont, Elvaloy® AM, which is a random terpolymer comprising ethylene, normal butylacrylate and glycidyl methacrylate (GMA). It is the GMA molecule that appears to be responsible for the reaction observed when the polymer is mixed with hot asphalt. This type of copolymer reacts with asphalt to form a polymer-linked-asphalt system with improved performance properties (Fig. 3).

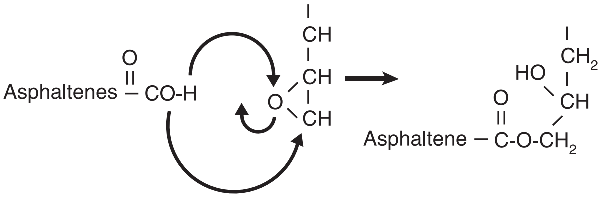

*Fig. 3. Proposed mechanism for reaction of EGA polymer with asphaltene molecule containing carboxylic acid group [18].*

For reactive compatibilization to occur in blends of polymers, there are four conditions that have to be met [16]:

- Sufficiently strong mixing to assure dispersion of one component in other
- The presence of reactive functional groups capable of reacting in the interface of the polymers
- The reaction should occur within the residence time of the polymers in the extruder, and
- The bonds formed should be stable to any further processing.

When considering the compatibilization process between asphalt and polymers, the above mentioned factors should also hold.

## ASPECTS THAT INFLUENCE THE PROPERTIES OF POLYMER-ASPHALT BLENDS

### Polymer characteristics

To be effective, a polymer must be blended with the bitumen and increase its rutting resistance at high temperatures without rendering it too viscous for the mixing procedure or too brittle at low temperatures. It should also be capable of being processed in asphalt conventional equipment [7]. The modifying polymer should be sufficiently compatible with the asphalt as not to cause phase separation during the storage, transportation, application and service.

Moreover, the modified polymer must be cost effective, *i.e.* the polymer should improve the rheology and strength of the asphalt with which it is mixed in such a way that any increased road costs imposed by its use are recovered through performance and reduced resurfacing costs.

Polymer content ranges between 2 and 10% by weight; however, the most common proportions were about 5 or 6% a few years ago. Now the polymer content has been reduced to 2 or 3%. Sometimes waste materials (due to their low cost they might be added in higher proportions), or mixes of two different polymers (as mentioned before) are being used [7].

Polymer parameters affecting the modification process include polymer content, chemical composition, structure, average molecular weight, molecular weight distribution, degree of branching, crystallinity, etc. [5, 7, 19].

For example, SBS type block copolymers should meet several requirements in order to be compatible with the asphalt. They should be rich in butadiene (about 60-70%) and the molecular weights of the styrene fraction must exceed 10,000 to obtain PS (polystyrene) rich domains [1].

Ali *et al.* [20] found that, at low temperatures, the mechanical properties of all paving mixtures seem to be affected primarily by the original grade of the asphalt used in making the binder, while the addition of the modifier is not statistically significant in adversely affecting low temperature stiffness. Thus, low temperature cracking should not be adversely affected by the addition of modifiers. However, as the temperature is increased, the stiffening effect of the modifier on the binder's properties increased, resulting in a significant increase in the modulus value of the mixtures, as compared to conventional paving mixtures. Thus, the use of modifiers can actually improve the temperature susceptibility of the binders.

### Asphalt characteristics

Asphalt nature greatly influences the binder micromorphology, as well as some of its properties, such as penetration and mechanical properties. It has also a very large influence on the stability of the blend [21].

As it has been mentioned numerous times, the polymer must be compatible with the bitumen and maintain this compatibility during storage and use. This is a difficult task, because the PMA constituents are very different in molecular weight and structure, viscosity and density [7].

Moreover, bitumen differences depend not only on the composition of the original crude, but also on the production process [14]. In all cases, there is a close connection between polymer type and bitumen composition, especially with the content of bitumen components, which act as solvents or swelling agents for the modifier [7, 19].

Even though not many studies have been made on the nature of the asphalt, some general conclusions have been drawn. An asphalt should contain enough oil fractions to dissolve and expand the polymer. It should also have a high content of condensed ingredients (*e.g.* aromatics hydrocarbons are often condensed and mix especially well with polar aromatic polymers) in order to guarantee the PMA blends endurance [22].

For a binder to be effectively modified, two cases have to be considered.

- In the first case, if the asphalt cement exhibits a high aromaticity, the polymer can be solubilized.
- In the second case, when the polymer is not soluble in the molecular sense of the term (elimination of all polymer-polymer interactions to replace them by polymer-solvent interactions), it can be swollen by the oily fraction of the asphalt.

For low polymer content, the continuous asphalt phase is enriched with resins and asphaltenes, thus leading to an increase in the consistency and the elastic properties of the binder. In general, a thermoplastic polymer modified asphalt (resulting from physical mixing of the constituents without chemical interactions between them) can consequently be regarded as a diphase system made up of a swollen polymer and a phase grouping the constituents of the asphalt not intervening in the solvation. If the polymer content is increased, the inversion point is observed. This transition is accompanied by a major modification in the physical properties of the blend. This results essentially in a significant increase in the plasticity interval, in tensile strength and elastic properties, and a reduction in thermal sensitivity over the utilization temperature range [23].

Studies by Vonk and Bull [24] have shown that when a thermoplastic rubber copolymer is in contact with bitumen, the elastomer absorbs, almost proportionally, all the bitumen components, with the exception of the asphaltenes. The asphaltenes, however, require support from the presence of the maltenes to avoid their precipitation. Thus, if the asphaltene content of the bitumen is too high, addition of a thermoplastic rubber can result in asphaltene precipitation or gelation and the blend becomes unworkable. Conversely, if the asphaltene content is low the polymer is able to absorb more maltenes after which even a single phase blend may be obtained.

When phase separation occurs in a bitumen-SBS material, the thermoplastic rubber phase rises to the surface of the bitumen and the asphaltene phase falls to the bottom. The top section of the mixture thus becomes soft and elastic, while the bottom becomes hard and brittle. The ratio of penetration at the top/penetration at the bottom quantifies the extent to which separation of the binder has taken place.

The softening point of the bitumen-thermoplastic rubber blends is largely governed by the aromaticity and average molecular weight of the base bitumen and tend to be little influenced by the hardness of the base bitumen. The viscosity of the blends at 180°C is predominantly affected by the average molecular weight of the base bitumen [5].

The asphaltene content of the bitumen-thermoplastic rubber blend must also be carefully balanced as, at low concentrations, the asphaltenes interact with the thermoplastic rubber molecules forming beneficial associations, which result in higher flow resistance and higher softening points. Conversely, a too high asphaltene content will result in phase separation leading to a lower proportion of the thermoplastic rubber being available in the continuous phase. The permissible level of the asphaltene concentration is dependent upon:

- polymer content
- polymer molecular weight
- asphaltene molecular weight
- aromaticity.

Careful balancing of the aromatic content and the aromaticity in relation to polymer content is necessary in order to produce a bitumen-thermoplastic rubber blend which is stable, and in which the thermoplastic rubber is present as a continuous phase to the maximum extent possible, in order to achieve the maximum possible benefit from the polymer. Such blends are termed as "compatible" blends [5].

## Mixing conditions

The parameters influencing the mixing process include [22]:

*Nature of the polymer.* The time required to achieve a homogeneous blend of the polymer and the asphalt will vary with the type of polymer, its molecular weight, and (for thermoplastic rubbers) with the chemical composition of the polymer. A higher molecular weight will give rise to longer blending times, and vice versa [5].

*Physical form of the polymer (powder, crumbs, pellets).* The physical form of the polymer influences the blending process in two ways. The smaller the particle size of the polymer, the lesser it has to be reduced in order to achieve a good dispersion. In addition, since smaller particle size means larger surface area per unit mass of polymer, penetration of the bitumen and swelling of the polymer is facilitated, and thus more rapid dissolution is completed. Powdered polymers will therefore disperse and dissolve more rapidly than porous pellets [5].

*Nature and grade of the bitumen.* Bitumen plays a complex role in the mixing process as both its composition and viscosity affect the blending process in more than one way. The way constituents affect the mixing process has not very extensively been studied, as has been mentioned before. General observations drawn included that an asphalt should contain big oil fractions to dissolve and expand the polymer, and a high content of condensed ingredients in order to guarantee the PMA blends endurance [22].

On the other hand, low viscosity bitumen is beneficial in aiding pre-dispersion of the polymer in the bitumen, and will subsequently speed the penetration and swelling of the polymer particles. A low bitumen viscosity at the blending temperature will improve the disintegration of the polymer at the mill and result in a more rapid particle size reduction [5].

*Type of mixing equipment.* Two main methods exist for the dissolution of polymer in the bitumen, high shear and low shear mixing. For low shear mixing a simple mixing tank with a paddle stirrer can be used with powdered modifier, the action being confined to the swelling and dissolving by the bitumen. The mixer serves to maintain homogeneity of composition and uniformity of temperature, proving little or no heat input itself.

In high shear mixing, polymer particles are physically reduced in size by mechanical and hydrodynamic shear in a rotor-stator combination accompanied by significant input of heat energy to the mix.

*Time-temperature profile during mixing.* The ideal mixing process should be undertaken at the lowest possible temperature for the shortest possible time, corresponding to the complete incorporation of the polymer into the bitumen both from an economic standpoint and to minimize any thermal effect on the polymer. In practical terms however, the time-temperature profile is a function of the bitumen chosen, and its requirement to achieve mobility and initial swelling of the polymer. For SBS, for example, temperatures higher than 190°C should be avoided to minimize thermal effects on the polymer [23].

Blending conditions have an important impact on the structure and properties of modified binders: the longer the mixing time, the finer the microstructure. There is however, a starting point beyond which polymer degradation leads to a decrease in mechanical properties and, more precisely, in low temperature deformation possibilities. The higher the temperature, the more rapidly this threshold is reached [23].

## Compatibility and Stability

A polymer may be incompatible, slightly compatible or compatible with bitumen.

- Incompatible polymers, when mixed with asphalts, result in heterogeneous mixtures without cohesion or ductility. The polymer affects the colloidal equilibrium of the asphalt and, therefore, the cohesion of the material.
- Slightly compatible polymers require special mechanical, thermal or chemical processes to successfully improve asphalts.
- Compatible materials yield physically stable blends, using conventional mixing techniques, and they may or may not improve the physical properties of the asphalt.

A proper degree of compatibility between polymer and asphalt is necessary in order to avoid separation during storing, pumping and application of the asphalts and to achieve the expected properties in the pavement. Poor storage stability will render the polymer modified asphalt unsuitable for use in paving binder applications, roofing applications, and other industrial specialty products.

The extent to which a stable system is formed when the bitumen is modified by the addition of thermoplastic rubber is dependent upon a number of factors which include:

- the amount and size of the asphaltenes
- the amount and size of the polymer molecules
- the aromaticity of the maltene phase.

The complexity of the inter-relationships between these factors can be seen in Fig. 4. Although the axes in this diagram are unscaled, it can be deduced that too high aromaticity should be avoided as this leads to a weakening of the polystyrene domains causing low softening points and low flow resistance. At low aromaticity levels, however, insufficient polymer will be incorporated into the bitumen, which also leads to low flow resistance [5].

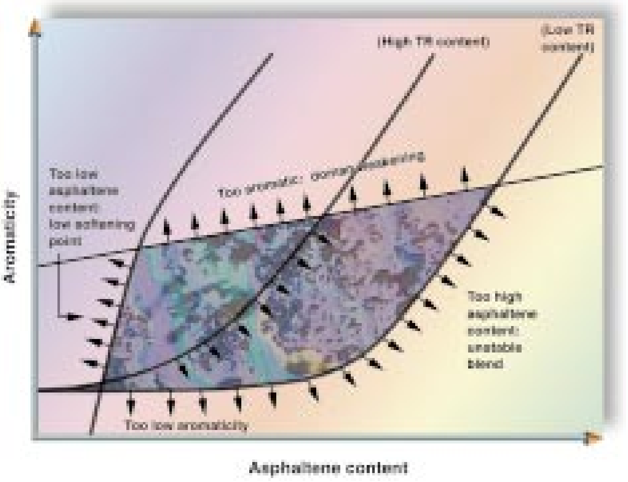

*Fig. 4. Influence of the asphalt constitution on asphalt/SBS blends [5].*

The compatibility and stability of the polymer-asphalt blends can be improved considerably by certain commercial compatibilization processes, such as the one patented by Exxon Research and Engineering Co. (Florham Park, NJ), where both the asphalt and the polymer are in contact with sulfonate or sulfonic acid groups and then blended. TexPar Energy, Inc. uses an additive called ButaphaltTM, among many others; for compatibility purposes, considers the addition of an acid after the polymer has been added to the asphalt. It has also been stated that the storage stability of asphalt can be improved, if the acid is added to the asphalt before the polymer. One example where an acid is added to improve the stability of the asphalt-polymer blend, is a technology patented by Ergon Incorporated (Jackson, MS).

It is also known that the stability of polymer-bitumen compositions can be increased by the addition of crosslinking agents such as sulfur, frequently in the form of elemental sulfur. It is believed that the sulfur chemically couples the polymer, and the bitumen through sulfide and/or polysulfide bonds. The addition of extraneous sulfur is required to produce the improved stability, even though bitumens naturally contain varying amounts of native sulfur.

UV microscopy is used to determine the completeness of blending and compatibility of polymer-modified asphalts. Samples are taken every hour as seen under a fluorescence microscope in order to see the degree in which polymer is incorporated in the asphalt. As mentioned before, finely dispersed polymer grains in the asphalt matrix would be considered a homogeneous (and therefore compatible) system. Fig. 5 shows a micrograph of a compatible system, which could be compared with an incompatible system shown in Fig. 6, where the mixture does not seem homogeneous.

In order to find out if phase separation or incompatibility is present, several approaches are accepted: phase compatibility, rheological changes and softening point variation. For this last test, PMA is poured into a metal toothpaste tube and left in an oven for three days at 160°C. Samples are then taken from the bottom portion of the blend and the top portion of the blend, and softening points between these two samples are compared. The difference between the softening point of the top portion and the softening point of the bottom portion shall not differ by more than 4°C. Any higher difference would suggest substantial phase separation (absence of storage stability). The same samples are also examined using fluorescence microscopy to compare their microstructures. For true stability, the top portion of the blend should have the same continuous phase as the bottom portion.

*Fig. 5. Compatible system with 4% SBS [5].*

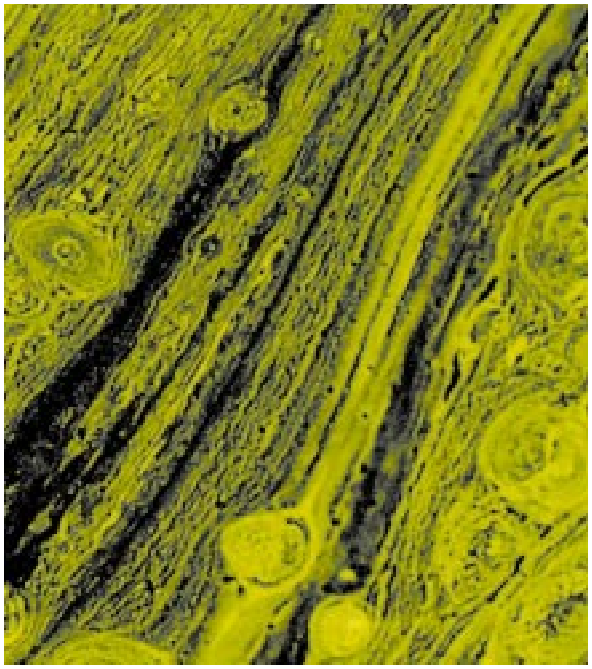

*Fig. 6. Incompatible system with 4% SBS [5].*

## RELATIONSHIPS BETWEEN BINDER PROPERTIES AND MIXTURE PERFORMANCE

Performance cannot be described by some ideal chemical functionality, but rather must be defined in physical terms corresponding to relative pavement life. In order to validate any test procedure chosen for a binder specification, a broad range of materials must be tested and then subjected to asphalt concrete evaluations under laboratory and field conditions which most closely mimic the expected failure modes (the so named "torture tests").

Several European highway agencies have even incorporated these laboratory types of tests into their asphalt concrete mix specifications. The French Central Highway Laboratory (LCPC) has developed a sophisticated wheel tracking device to predict permanent deformation and has built a large, heavy-duty carousel to simulate load-related fatigue damage. In Hamburg, Germany, a modified version of a British wheel tracking device has been used for its hot mix specifications for almost twenty years. A virtual elimination of their rutting problems has been claimed.

The mixing temperature of aggregates with asphalts must be chosen based on the binder viscosity. The fact that polymer modified asphalts are pseudoplastic fluids, and they can therefore successfully be mixed at lower temperatures, must be taken into account [25].

As has been mentioned before, polymers can be used effectively to improve high temperature performance, but larger amount of polymer is not always better, at least from a cost effective standpoint. Once the binder reaches a certain stiffness, additional polymer has only a marginal effect on rutting resistance as measured by the French tester. This conclusion must be tempered, however, by results from the German wheel tracking device. When moisture damage and hydrostatic pressures are added to the equation, additional polymer may prove to be most beneficial, especially for softer asphalts [25].

Classic consistency tests for asphalt binders such as penetration, absolute viscosity, kinematic viscosity, and ring and ball softening point do not adequately predict results from laboratory rutting simulators, when polymer modified asphalts are used as the binder; neither do these tests correlate well with the stiffness or viscosity parameters as determined by dynamic mechanical analysis. There is a clear tendency for the conventional static load test to overpredict the stiffness, and, hence, the expected benefit of the modified binder [25].

Some attempts have been made to develop reasonable correlations between rutting and the traditional measurements of consistency, but they require numerous empirical parameters, which are only valid within certain constraints such as crude type and polymer type; so these correlations have virtually no real significance.

Results from dynamic rheological tests seem to correlate well with the wheel tracking device results, as it was shown in a study done by King *et al.* [25]. They concluded that the choice of temperature and frequency is critical if dynamic rheology is to be used as a tool for predicting high temperature pavement performance. However, it is important to mention that the complete rheological master curves with shape factors are usually sufficient to compare asphalt quality, but they can only predict performance if they are compared under conditions where failure might be expected to occur [25].

## VENEZUELAN POLYMER MODIFIED ASPHALTS

Venezuelan heavy crudes are well known for their high quality (high asphaltene content and high asphalt yield). Actually, Venezuelan asphalts are among the most valued internationally. The overall demand for Venezuelan asphalts, as part of the international market, is obviously affected by the population and demographic trends, growth in the economy and the level of public infrastructure spending. In addition, as asphalt is a petroleum derivative, oil industry dynamics and environmental legislation also influence the demand. For the case of modified asphalts for paving applications, which is a market with only foreign clients, the demand is also affected by the climate of each region in four-season countries [26].

By reviewing the formal literature, it is difficult to find reports on a particular asphalt system. However, Venezuelan asphalts are frequently mentioned due to their high performance, especially for paving applications.

A research group in Universita di Trieste, Italy [27], has specifically worked with several Venezuelan asphalts, such as Laguna, Tía Juana and Bachaquero. They mentioned that a parameter that may indicate polymer-asphalt compatibility is the relationship between the asphaltene/resins ratio and the saturates/aromatics ratio. However, this relationship is not enough to assure the success of the polymer-asphalt blend. The stability and homogeneity of the blend is highly dependent on the ratio between the molecular weight of the asphaltenes and that of the resins. Bachaquero asphalts tend to have a high value of this ratio, as compared with other asphalts (including Laguna and Tia Juana). That could predict difficulties in the blending.

ERGON is a company that produces a PMA named “Sea-O-Flex“, in the US. Among other asphalts, ERGON has used Bachaquero asphalts to produce Seal-O-Flex and reports that very good commpatibilization and high performance are obtained with this asphalt and by using their proprietary technology.

On the other hand, Collins *et al.* [28] compared two asphalts from Shell (Martínez and Deer Park) with the Venezuelan Boscán asphalt. Their results indicate that Boscán is considerably less compatible with SBS than the other two asphalts. At a microscopic level, it shows a heterogeneous dispersion of the polymer and no polymer network is formed.

However, from previous work done at PDVSA-Intevep, the high level of compatibility shown by the Shell research group must be particular of the mixing conditions, and the polymer and the asphalt samples for their experiments. Morphologies showing more compatible systems had been obtained with Boscán asphalts at Intevep laboratories. Boscán forms a highly elastic system, and the SBS-modified sample has the highest elastic modulus of all the blends studied by them, which is explained by the high elastic moduli of neat Boscán asphalt [29].

King *et al.* [25, 30] used the Venezuelan asphalt from Laguna (they defined Laguna as a "Venezuelan crude, which yields high quality bitumen"). Laguna was vacuum distilled to produce four straight-run penetration grade asphalts (40/50, 60/70, 80/100, and 180/200). Each of these four grades was then modified with a styrene-butadiene block copolymer chemically reacted *in-situ* with the asphalt. A seven laboratory multi-national research project was launched to define which binder test methods could best serve as performance indicators, and more importantly, to determine how the asphalt grade and polymer concentration could be selected to most effectively meet specific requirements. However, comparisons about the performance of modified Laguna asphalt with other modified asphalts were not made.

It is also worth mentioning that currently CITERCO (a joint venture between CITGO Asphalt and ERGON Inc.) produces and commercializes polymer modified asphalts using Boscán and Bachaquero asphalts. Nynas Petroleum produces polymer modified Laguna asphalts.

## FINAL REMARKS

Modification of asphalt with polymers is considered the best option to improve asphalt properties. Polymers increase considerably the useful temperature range of the binders.

Most common asphalt pavement defects are: rutting (permanent deformation), thermal fatigue, stress fatigue and aging. To overcome these disadvantages, asphalt modification by polymer addition has been used.

The possible limitations with modified bitumens are:

- Cost increase
- Possible compatibility and stability problems
- Some difficulties may arise in the storage of the bitumen, mixing temperatures, and the length of time the material is held at elevated temperatures before laying.

Traditionally the incorporation of polymers into asphalt increased the price of the product between 60 and 100%, but,

- Polymer prices tend to decrease
- Polymer content tends to decrease
- The life cycle of the pavement or roof tend to increase up to ten times when using polymers.

SBS is the most used polymer to modify asphalts, followed by reclaimed tire rubber.

Among Venezuelan asphalts, the most used in laboratory studies are Laguna, Boscán and Bachaquero.

## References

1. Lewandowski, L.H. Polymer Modification of Paving Asphalt Binders. *Rubber Chemistry and Technology*, 67(3): 447, July-August, 1994.
2. Brûlé, B. Polymer Modified Asphalt Cement Used in the Road Construction Industry: Basic Principles, Transportation Research Board. *75th Annual Meeting.* Jan. 7-11, 1996, Washington, D. C., Paper No. 960167.
3. The Gale Group [on-line]. Polyphalt sees increased royalties, project revenve boost. *Rubber & Plastics News*. 30(20): 6. (25-05-2001).
4. The Freedonia Group. *Asphalt Products and Markets*, Weiss, D. and Billings, J. A. (directors), Industry Study 771, March 2000.
5. Morgan, P.; Mulder, A. *The Shell Bitumen Industrial Handbook*. Shell Bitumen, Surrey, 1995.
6. Becker, Y.; Muñoz, A.; Bolívar, R. *Asfaltos para pavimentación: Asfaltos modificados con polímeros*, Tech. Report INT-02931,94, Intevep, S.A., Los Teques, October 1994.
7. Giavarini, C. *Polymer-Modified Bitumen, Asphaltenes and Asphalts*, 1. Developments in Petroleum Science, 40, 381.
8. Heshmat, A.; Lewandowski, L.; Little, D. Polymer Modifiers for Improved Performance of Asphalt Mixtures. *Seminar organized by the Journal of Elastomers and Plastics and sponsored by the Programme Division Technomic Publishing AG.*, Basel, Switzerland, 1995.
9. Isacsson, U.; Lu, X. Testing and Appraisal of Polymer Modified Road Bitumens - State of the Art. *Materials and Structures*, 28:139, 1995.
10. Daly, W. H.; Qiu, Z.; Youngblood, J.; Negulescu, I. Enhancing Reinforcement Effects of Polymers in Asphalt: An Applied Approach to Solid Waste Disposal. Prog. Pac. Polym. Sci. 3 *Proc. Pac. Polym. Conf.* 3rd, 381, 1994.
11. Zielinski, J. Investigations on Thermal Properties of Asphalt-Polymer Compositions. *Erdöl und Kohle*, 42 (11); 456, November 1989.
12. Defoor, F. Physico-chemical Aspects of Asphalt Modification for Road Construction. *American Chemical Society Division of Rubber Chemistry*, May 15, 1990. Paper No. 15,
13. Serfaas, J-P.; Joly, A.; Samanos, J. SBS-Modified Aphalts for Surface Dressing- A Comparison Between Hot-Applied and Emulsified Binders. In: *Polymer Modified Asphalt Binders*, ASTM ST 1108, K. R. Wardlaw and S. Shuler (eds.), American Society for Testing Materials, Philadelphia, 281, 1992.
14. Giavarini, C.; Santarelli, M. L.; Braga, V. Progettazione di un polimero a base polipropilenica adatto per la modifica dei bitumi. *Chimica e l'Industria*, 75(4): 270, 1993.
15. Kelly, K. P.; Butler; J. R. Method of Preparation of Stable Bitumen Polymer Compositions. *US Patent 6 180 697*, Fina Technology, 1999.
16. Hayner, R. E. *Sulfur in Oil Asphalt and Polymer Composition and Process*, Marathon Ashland Petroleum LLC, 1999.
17. Baumgardner, G. L.; Burrow; M. R. Asphalt Compositions and Methods of Preparation Thereof. *US Patent 6 031 029*, Ergon Incorporated, 1997.
18. *http://www.dupont.com/asphalt/link1.html* (July 25th 2001).
19. Bellio, E.; Patti, N. Polimeri da riciclo come modificanti per bitume. *Macplas*, 17(144): 37, December 1992.
20. Ali, N.; Zahran, S.; Trogdon, J.; Bergan, A. A Mechanistic Evaluation of Modified Asphalt Paving Mixtures, *Canadian Journal of Civil Engineering*, 21:954, 1994.
21. Dony, A.; Durrieu, F. Influence de la nature du bitume sur les propriétés et la stabilité des liants bitumes-polymères. *Bulletin de Liaison des Laboratoires des Ponts et Chaussées*, 57, July-August 1990.
22. Zielinski, J.; Bukowski, A.; Osowiecka, B. An Effect of Polymers on Thermal Stability of Bitumens. *Journal of Thermal Analysis*, 43(1):271, 1995.
23. Brûlé, B.; Brion, Y.; Tanguy, A. Paving Asphalt Polymer Blends: Relationships Between Composition, Structure and Properties. Asphalt Paving Technology: *Proc. Association of Asphalt Paving Technologists, Technical Sessions*, 57:41 (1988).
24. Vonk, W. C.; Bull, A. L. Phase Phenomena and Concentration Effect in Blends of Bitumen and Cariflex TR. *VII Intl Roofing Congress*, München, Germany. May 30 - June 1 (1989).
25. King, G. N.; King, H. W.; Harders, O.; Chavenot, P.; Planche, J-P. Influence of Asphalt Grade and Polymer Concentration on the High Temperature Performance of Polymer Modified Asphalt. *Asphalt Paving Technology: Proc*. Association of Asphalt Paving Technologists, Technical Sessions, 61:29, 1992.
26. The Freedonia Group. *Asphalt Products and Markets*, Weiss, D. and Billings, J. A. (directors), Industry Study 771, March 1996.
27. G. Costantinides, C. Loni, and N. Schromek. Mescole di bitume con differenti polimeri *Riv. Combustibili*, 40, 105 (1986).
28. Collins, J. H.; Bouldin, M. G.; Gelles, R.; Berker, A. Improved Performance of Paving Asphalts by Polymer Modification. *Asphalt Paving Technology: Proc*. Association of Asphalt Paving Technologists, Technical Sessions, 60:43, 1991.
29. Rodríguez, Y.; Blanco, P.; Gabay, R.; Torres, N.; Castañeda, R. *Evaluation of Compatibility of Boscán Asphalt with Polymers* Tech. Report INT-3956, 1997, Intevep, S.A., Los Teques, October 1997.
30. King, G. N.; King, H. W.; Harders, O.; Arand, W.; Planche, P. P. Influence of Asphalt Grade and Polymer Concentration on the Low Temperature Performance of Polymer Modified Asphalt. *Asphalt Paving Technology: Proc*. Association of Asphalt Paving Technologists, Technical Sessions, 62:1, 1993.

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