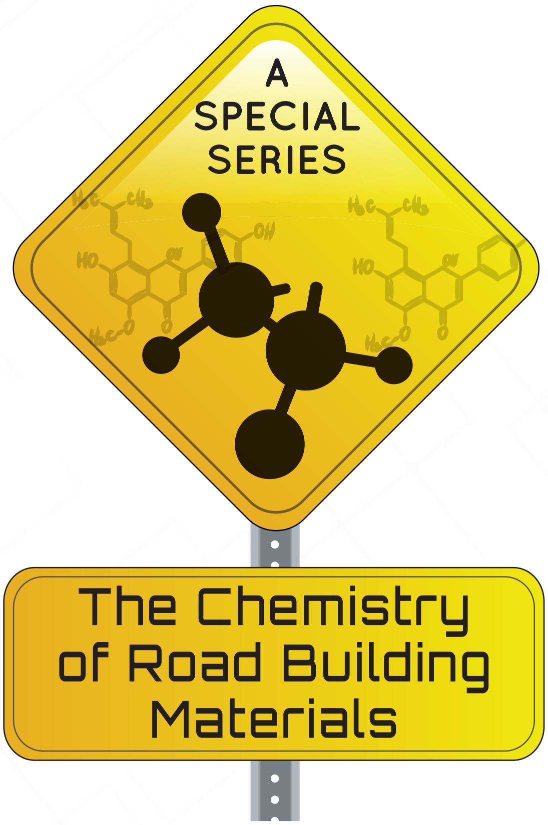
by Tom Kuennen Contributing Editor



Asphalt a la Carte

Modifiers Control Mix Performance

Petroleum (literally, rock oil) is one of the most important gifts of the union of carbon and hydrogen. But instead of being a simple compound (like water), petroleum is a natural product, a complex "soup" of thousands of hydrocarbon compounds, the mix varying according to source. The never-ending variance of the makeup of petroleum challenges the refiner, who must adjust the refining process to optimize extraction of the valuable components of petroleum.

Liquid asphalt binder might be thought of as the sludge left over from petroleum after higher-revenue products such as gasoline, plastic feed stocks, kerosene and petroleum distillates have been removed. About 3 percent of a barrel of petroleum (42 gallons) winds up as liquid asphalt.

"Asphalt literally is the bottom of the barrel," says Codrin Daranga, Ph.D., technical manager, Blacklidge Emulsions. "It is the waste left over at the bottom of the distillery after more valuable hydrocarbons have been extracted. At one time refineries would give away the liquid asphalt for the price of transportation, just so they would not have to deal with it. Now there is such a need – with so little liquid asphalt available – that we pay top dollar for it."

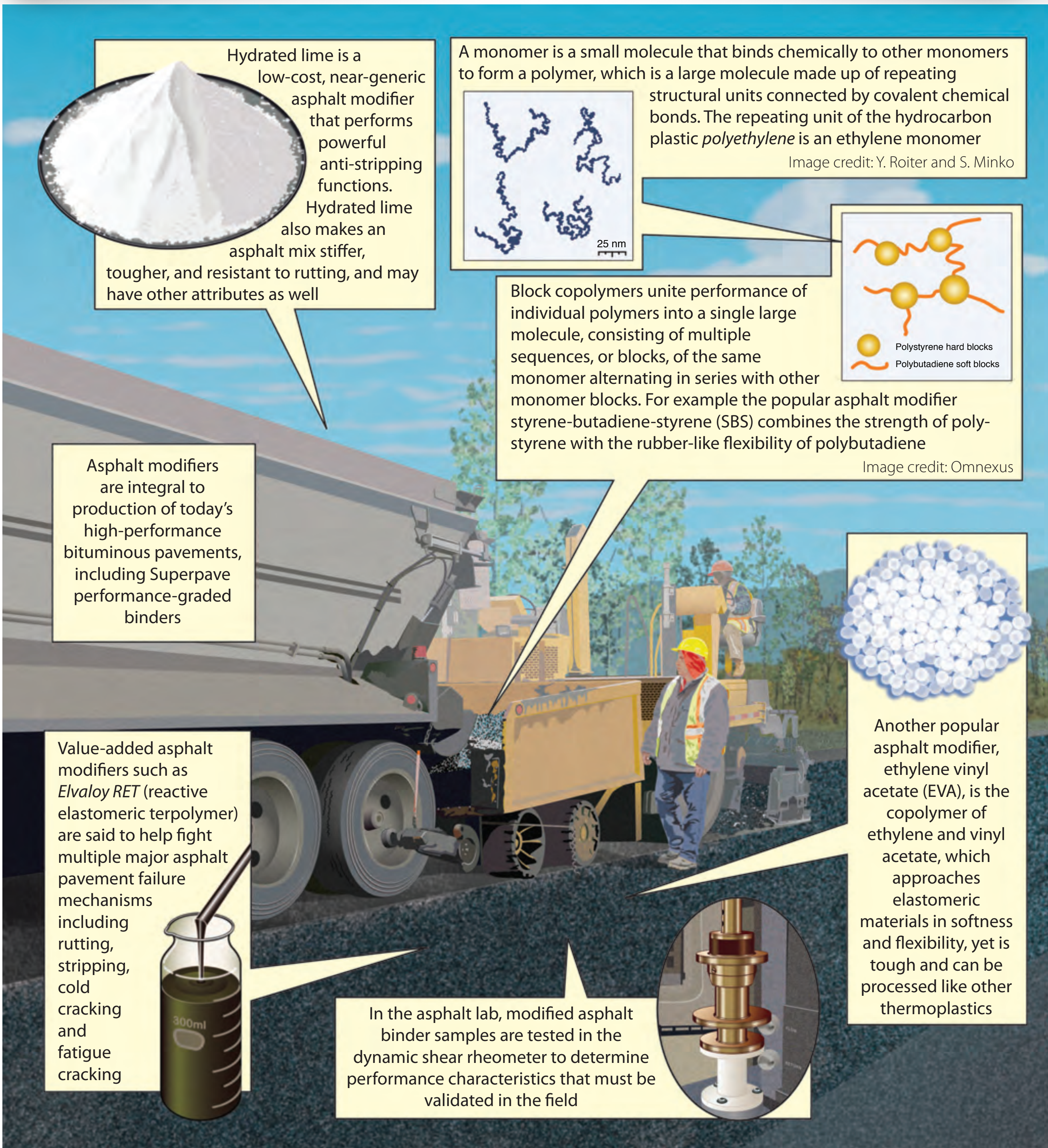
As the demand for gasoline and plastics have increased, refineries have gotten better at removing those "light" products from the source crude. As those value-added products are removed, the "richness" of what's left over as liquid asphalt is diminished.

"The industry has gotten better at refining petroleum," Daranga says. "It stands to reason that more valuable product has been extracted than ever before, and there is less in the remaining liquid asphalt. But it depends on the refinery. Some refineries are geared almost entirely to making gasoline; that's what they're designed to do. There will be very little asphalt from those plants, and it won't be very good. For them asphalt is a waste and they will do everything they can to minimize that waste.

"But there is another kind of refinery that is geared only toward making asphalt," Daranga says. "Its business model is to make asphalt, so that end product will be quite good." Such a dedicated refinery in Louisiana is scheduled to come online this year.

"Without a doubt, over the last 20 to 30 years, refiners have gotten better at extracting all the high-value materials they can out of the source crude," says Bob Kluttz, senior scientist, research and development, Kraton Polymers. "This includes a variety of technologies, different distillation and extraction techniques as well as coking. You can take asphalt that once was $100 to $200 a ton, and turn it into light ends and gasoline which sell for much more."

April	May	June	July	August	September	October
THE CHEMISTRY OF ASPHALT MODIFIERS	THE CHEMISTRY OF CONCRETE ADMIXTURES	THE CHEMISTRY OF ASPHALT EMULSIONS	THE CHEMISTRY OF AGGREGATES	THE CHEMISTRY OF LOW-ENERGY MIXES	THE CHEMISTRY OF RECYCLED/ RECLAIMED MATERIALS	THE CHEMISTRY OF PAVEMENT FORENSICS



Hydrated lime is a low-cost, near-generic asphalt modifier that performs powerful anti-stripping functions. Hydrated lime also makes an asphalt mix stiffer, tougher, and resistant to rutting, and may have other attributes as well

A monomer is a small molecule that binds chemically to other monomers to form a polymer, which is a large molecule made up of repeating structural units connected by covalent chemical bonds. The repeating unit of the hydrocarbon plastic *polyethylene* is an ethylene monomer

Image credit: Y. Roiter and S. Minko

Block copolymers unite performance of individual polymers into a single large molecule, consisting of multiple sequences, or blocks, of the same monomer alternating in series with other monomer blocks. For example the popular asphalt modifier styrene-butadiene-styrene (SBS) combines the strength of poly-styrene with the rubber-like flexibility of polybutadiene

Image credit: Omnexus

Asphalt modifiers are integral to production of today's high-performance bituminous pavements, including Superpave performance-graded binders

Another popular asphalt modifier, ethylene vinyl acetate (EVA), is the copolymer of ethylene and vinyl acetate, which approaches elastomeric materials in softness and flexibility, yet is tough and can be processed like other thermoplastics

Value-added asphalt modifiers such as *Elvaloy RET* (reactive elastomeric terpolymer) are said to help fight multiple major asphalt pavement failure mechanisms including rutting, stripping, cold cracking and fatigue cracking

In the asphalt lab, modified asphalt binder samples are tested in the dynamic shear rheometer to determine performance characteristics that must be validated in the field

Individual refiners also are using a wider variety of crudes, and this has led to increased variability of asphalt. "There are well over a hundred crude oil fields that are being accessed in North America, and each one is chemically a little different, so the asphalt you make out of it is chemically different," Kluttz says. "They each will respond somewhat differently to modification. Consistency is the issue. The binder supplier's concern is having that tanker show up day after day and having exactly the same material in it, month after month."

One asphalt contractor was quite blunt about the situation. "The quality of the available liquid asphalt has changed," he told *Better Roads*. "The asphalt is not as good as it used to be, in my opinion. That all changed as plastics evolved. We're trading plastic water bottles for good asphalt, and now we're adding plastic and rubber back to the mix."

Polymer Modifiers for Asphalt

That contractor is describing the trend to add polymer modifiers to liquid asphalt to improve its performance.

"The asphalt binder supplier buys liquid asphalt from the refinery and creates a value-added product by improving, modifying or chemically changing that asphalt," Daranga says. "That can happen by adding ground rubber from tires, or adding classical – or not-so-classical – polymer modifiers."

Basically there are two types of polymer modifiers: elastomers and plastomers. Elastomers increase modulus (stiffness) and also give the asphalt elasticity and stretchiness. Under load it can provide recovery under deflection. Plastomers are more limited in that they just stiffen the asphalt, so they don't provide the kind of recovery you get with an elastic material, but still may be best suited for a particular application.

A monomer is an atom or a small molecule that binds chemically to other monomers to form a polymer, which is a large molecule made up of repeating structural units connected by covalent chemical bonds.

"A monomer is 'one' piece, an individual molecule," Kluttz says. "A polymer is a bunch of monomers connected together. For example, a molecule of butadiene has only four carbons, but we can hook together a thousand of those end to end to make a polybutadiene chain that's then 4,000 carbons long. We then hook polystyrene chains to each end of that. The result is a block polymer, which has blocks of polystyrene, and blocks of polybutadiene."

Adding flexibility and strength to liquid asphalt by dissolving long-chain polymer molecules in it will improve the asphalt, Daranga says. "We will add different kinds of polymers, most commonly styrene-butadiene-styrene (SBS), but there is a huge choice of polymers for modification."

Imagine a chain in which the links are monomers, Daranga says. "Polymer describes multiple monomers linked in a long chain," he says. "All the chain links can be the same, or you can have two different kinds of chain links. The way you put them together opens up a whole world of possibilities. You can put them together one after the other, as in A-B-A-B-A-B. You can put them together as all As, and when you run out of those, all Bs. They can be assembled in a completely random or statistical fashion, or fancy patterns, AAA-BB-AAA-BB.

"SBS is just that," Daranga told *Better Roads*. "It implies you have three blocks, SSS-BBB-SSS. But the chemist also can vary the length of the blocks and the ratio between them makes a huge difference in properties. SBS is a tri-block copolymer."

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The beauty and popularity of the SBS modifier comes from its union of the hard monomers of styrene – which provides stiffness and strength (think strong polystyrene plastic children's toys) – with the flexibility of polybutadiene (think synthetic rubber).

"The best way to visualize an SBS molecule is as a nunchuk," the Okinawan martial arts weapon, Daranga says. "You have two sticks with a flexible link in between them. The styrene is the stick and the butadiene is the flexible link, but not like a chain, instead like a rubber band. They also have the ability to stack one on top of the other, and create crystal-like domains. If you have a bunch of these molecules and put them together, they will try to stack up in a fashion almost like cross-linking, but it's a physical, temperature-driven process that you can reverse by melting those crystal-like domains."

The process is similar to vulcanization of rubber, where the rubber molecules or components are tied together with very strong sulfur bonds. "The same thing happens with SBS when it cools off," Daranga says. "If it cools enough, and those styrene chains are close enough, they will pack together in a similar but weaker fashion to create a network, only not as strong as in a tire."

"SBS polymers are probably the most common modifier used in paving globally," Kluttz says. "What's special about SBS – why it works so well – is that it's a combination of two different polymers. It's a block polymer, so it has blocks of polystyrene, and blocks of polybutadiene. When you mix SBS polymer into hot asphalt, it completely dissolves into a homogeneous liquid. But when it cools back down, the polystyrene domains come back out and come together to give the liquid asphalt increased stiffness or modulus."

Modern PG binder specs sometimes also have an elastic recovery spec. "In the lab you stretch it out and it has to recover 60 or 70 percent of its original length," Kluttz says. "Asphalt has near-zero elastic recovery, and for most of the binders today, we're only putting in 2.5 to 3 percent polymer. So how does that little bit of polymer give that much 'stretchiness' to the asphalt?

"What happens is that the polybutadiene rubber polymer looks a whole like the light ends of asphalt," Kluttz answers. "The polymer literally soaks up the light ends of asphalt – the nonpolar saturates and aromatics -- so the 2 to 3 percent effectively becomes 20 or 30 percent, with the polymer swelling like a sponge soaking up water."

Thus, in an SBS-modified asphalt pavement, the polystyrene adds strength while the polybutadiene adds flexibility and elasticity. "Styrene helps control the organization of the butadiene," Daranga says. "If I just put the elastic parts in there, they would float all over the place, looking like a ball of spaghetti. But if I can tie the spaghetti here and there with the crystal-like structure provided by the styrene, that's much better."

A related, popular polymer modifier is SBR. "If SBS is styrene-butadiene-styrene, then SBR is styrene-butadiene-rubber," Kluttz says. "They are similar, but not exactly the same. With SBR, the styrenes and butadienes are all mixed together, randomly, compared to SBS, which as a block copolymer is organized in blocks."

While SBS is supplied to the liquid asphalt supplier in small, solid pellets, and has to be dissolved in the liquid asphalt using mixing equipment, SBR is a liquid latex, which can be injected into the liquid asphalt by the binder supplier or at an asphalt plant.

It's supplied in drums, tankers or even rail cars. These products will be 30 percent water, compared to SBS which are pellets. If blended into an emulsion for surface treatments, SBR may be cationic or anionic to enhance performance with existing aggregates.

Ethylene-Based Polymers

Another popular family of polymer modifiers are the cyclic ethylene-based polymers, and the pure ethylene-based polymers like ethylene-vinyl-acetate (EVA).

EVA is the copolymer of ethylene and vinyl acetate. The weight percent of vinyl acetate usually varies from 10 to 40 percent, with the remainder being ethylene. As a plastomer it's a polymer modifier but it doesn't have the "stretchy" properties of an elastomer. EVA is says to be an older technology, but it still can be used to bring liquid asphalt up to a PG rating.

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– Codrin Daranga, Ph.D., technical manager, Blacklidge Emulsions

That's because EVA is a polymer that approaches elastomeric materials in softness and flexibility, yet can be processed like other thermoplastics. EVA typically is added at concentrations between 2 to 5 percent by weight of asphalt binder, and is typically dispersed to the hot asphalt binder at temperatures between 300 to 340 degrees F.

"Benefits of this polymer modifier include the fact that only moderate agitation is necessary," says blending equipment manufacturer Ecopath Holdings. "The blends can be stored for weeks without succumbing to separation. Consistent with many other polymer modified asphalts, the compatibility of the EVA and asphalt binder is vital for achieving the desired properties."

Studies have shown that at lower polymer contents (3 percent by weight), EVA modified binders exhibit dispersed polymer particles in a continuous bitumen matrix, Ecopath reported. "EVA modified binder properties, such as morphology and storage stability, are influenced by the characteristics of the base bitumen and binders," Ecopath says. "Generally, increases in EVA concentration yield greater improvements in the binder; however, these increases also lead to reductions in storage stability. Other studies have shown that, when EVA and SBS modified binders are compared to neat binders, SBS binder exhibits a significantly higher elastic recovery than neat binders. Also, EVA binders tend to exhibit fewer improvements in elastic recovery while losing ductility and elastic recovery at a greater rate."

And that's not all. "There are chlorinated polyethylenes, oxidized polyethylenes and polypropylenes," Blacklidge Emulsions' Daranga says. "Depending on how long or short the molecules are, you get into the waxes or paraffins. There are ring-based polymers such as DuPont's *Elvaloy*. Cellulose-based polymers can be used as reinforcers. The possibilities are limited only by our imagination."

Response to Superpave

The advent of the PG binder rating system after the first Strategic Highway Research Program (SHRP) and the Superpave system of asphalt mix design was the prime driver of the current interest in asphalt modifiers.

"It definitely highlighted the need for us to modify asphalt to get the better-performing binder properties that we needed out of the same old asphalts we were using," Daranga says.

Polymer modified binders have allowed the use of techniques previously not practicable, such as microsurfacing and use of asphalt emulsion chip seals on high-volume roads. And specifying agencies are finding that many of the Superpave binder grades require polymer modification to concurrently meet the requirements for high temperature resistance to rutting, and low temperature resistance to thermal cracking.

"Superpave did a lot to accelerate modified asphalts," Kluttz says. "Up to then we just had pen-graded asphalts, and viscosity-graded asphalts. Both those parameters were generic single-points, so pretty much any crude source could produce straight run asphalt to meet most of the required pen and viscosity grades. Most of the states were developing their own tests and requirements to make sure polymers were included, but the Superpave specs to some degree built that in using the temperature range."

Photo courtesy MWV Evotherm

In central California, terminal blend of rubberized asphalt liquid is injected into production of warm mix asphalt

That didn't capture everything. When Superpave came out the majority of the states, even today, have kept some or all of their additional tests they use, along with Superpave, like elastic recovery, the most common one. They've maintained those tests to give them the performance they expect out of polymer-modified asphalt, the so-called Superpave Plus specs.

"The liquid asphalt cement by itself is a material that is not very easy to work in ambient conditions, but value can be added to the asphalt," Daranga says. "The typical asphalt that comes from the refinery has only a certain useful temperature interval, that is, the temperature limits during which that particular material can most probably perform without failure. Quite often that range of temperature is too narrow, and lots of times we will need to 'stretch' it, or expand it to allow it to stand up to heavy traffic loads or the weather. The only way we know how to do that today is by adding compounds that enhance that ability."

The Missouri experience demonstrates the embrace of modified asphalts in the post-Superpave climate. In a presentation at the 2011 conference of the Association of Modified Asphalt Producers – *Missouri's Full Depth Pavement with Modified Binders* – MoDOT's state construction and materials engineer Dave Ahlvers says in 2000 the Show-Me State placed just 2,800 tons of polymer modified asphalt mix on two centerline miles of major roads. But in 2006, the state placed 3 million tons of polymer modified mix on 1,500 centerline miles of major roads. "MoDOT is willing to pay more for polymer modified asphalt to provide a longer lasting pavement," Ahlvers says.

Mineral Modifiers and Extenders

There are many kinds of asphalt modifiers or additives other than polymer modifiers. These can include mineral modifiers such as hydrated lime, fly ash or portland cement; a liquid mineral additive, polyphosphoric acid (PPA); and extenders like sulfur, itself often a product of petroleum refining.

The more familiar polymer modifiers mix or dissolve with the liquid binder to help it perform better. Mineral modifiers perform physically to enhance adhesion of binder to aggregate, or keep liquid asphalt binder from draining from an aggregate structure, as with stone matrix asphalt.

Hydrated lime is pre-eminent among the modifiers used principally to fight moisture damage to asphalt pavements. Moisture damage – the loss of strength and stiffness of the mix due to water being present in different forms or phases – is a syndrome that can threaten long-term durability of asphalt pavements.

Moisture can penetrate in the liquid phase from the surface, rise via capillary action from the base, and also diffuse in the vapor phase throughout the pavement structure. This water can cause a loss of adhesion of the asphalt binder to the aggregates, resulting in the condition known as stripping.

One view is that in the presence of moisture, stripping is driven by the aggregate surface's affinity for water. Mineral- or polymer-based additives can change the surface of the aggregate from hydrophilic (water-loving) to hydrophobic (water-hating). Simply put, some aggregates prefer water over asphalt, tending to be acidic and suffer from stripping after exposure to water. Other aggregates prefer asphalt to water, tend to be basic (versus acidic) and tend not to suffer from stripping.

In the presence of hydrophilic aggregate, liquid antistrips and polymers are added to asphalt binder, while dry antistrips like hydrated lime, portland cement or fly ash are added to the aggregates. They operate by boosting adhesion between aggregate surface and binder, by reducing binder surface tension and thus helping the binder more completely enrobe the aggregate particles, or improving the chemical properties of both.

Polyphosphoric Acid

Polyphosphoric acid, or PPA, despite its name beginning with "poly, is not a polymer. "The longest PPA chain with the same units repeating are in the neighborhood of five or six units," says Blacklidge Emulsions' Daranga. "To be a polymer you need to be at least in the neighborhood of 50."

Furthermore, PPA is an inorganic compound, so it is not hydrocarbon-based. It's an inorganic acid, just like hydrochloric acid. It modifies properties of asphalt, bringing subpar binder up to a PG level. "Its method of activity is elusive and it's difficult for us to understand exactly how it works," Daranga says. "For this reason some agencies are afraid of it. But contractors would like to use it because it's not expensive."

Polyphosphoric acid has been proven as a successful modifier for asphalt either by itself or in combination with polymers, but the word on its performance needs to penetrate the public agency level, says Darrell Fee, Rene Maldonado, and Henry Romagosa, ICL Performance Products, and Gerald Reinke, Mathy Construction, in their 2010 Transportation Research Board paper, *Polyphosphoric Acid Modification of Asphalt*.

"In fact, over the past five years, an estimated 3.5 to 14 percent of the asphalt pavement placed in the United States contained PPA," they says. "This represents up to 400 million tons of asphalt mix. However, for any particular pavement project, the information on the use of PPA remains largely in the private sector. The information in the public sector is mainly limited to laboratory studies of asphalt modified with PPA. There are only a few reports on the field performance of asphalt containing PPA or polymer and PPA, primarily from the test tracks at National Center for Asphalt Technology (NCAT) and The Minnesota Road Research Project (MnROAD). Due to the lack of data in the public domain, there are concerns about the moisture sensitivity of PPA modified asphalts."

The mechanism by which polyphosphoric acid interacts with asphalt to improve rheology and other properties is still under investigation, the authors says. "One theory suggests that polyphosphoric acid reacts with various functional groups in the asphalt, breaking up the asphaltene agglomerates and allowing the individual asphaltene units to form a superior dispersion in the [surrounding] maltene phase. Once dispersed, the individual asphaltene units are relatively more effective in forming long-range networks and affecting the rheology and physical characteristics of the asphalt."

In neat asphalt, polyphosphoric acid generally increases the high temperature PG grade while generally maintaining the low-temperature properties, depending on the asphalt, Fee, Maldonado, Reinke, Romagosa says. "The high-temperature PG grade usually increases linearly with PPA addition," they says. "As would be expected when the high temperature PG grade increases, the binder viscosity increases and DSR [dynamic shear rheometer] phase angle decreases. These effects can be seen across most asphalts, but the strength of the response is asphalt-dependent."

Sulfur is being marketed as an extender to asphalt that provides a more durable pavement. One variation is a mixture of sulfur with pelletizing agents and agents designed to reduce emissions in which sulfur subsititutes for a very high percentage of liquid asphalt, from 20 to 40 percent of the asphalt. It results in a much stiffer binder and mix, and the expectation is that it will have improved rutting and fatigue resistance. The sulfur crystallizes and turns into a hard solid, so it becomes closer to a component of the aggregate, resulting in high stiffness or modulus.

Crumb Rubber Modifier

Asphalt rubber, or rubberized asphalt, is a chemically reacted mix of liquid asphalt binder with 15 to 22 percent crumb rubber obtained from reclaimed tires and added to liquid asphalt. It is reacted at elevated temperatures prior to being mixed with aggregate.

This so-called wet process, in which the rubber crumbs react with the liquid asphalt, differs from the dry process, in which asphalt crumbs are added with the aggregate.

Rubberized asphalt is a generic term describing any kind of rubber placed in any kind of asphalt. But the term asphalt rubber is quite specific being defined by the American Society for Testing and Materials as 15 percent ground tire rubber combined with liquid asphalt and other additives.

Asphalt rubber has been used both in hot-mix applications and in spray surface treatments. The latter include chip seals, stress-absorbing membranes, and stress-absorbing membrane interlayers. The enhanced performance of asphalt rubber reduces the overlay thickness needed in a given application, preserving grades and conserving clearances next to curbs and medians.

Currently, most crumb rubber-modified binder used in hot-mix asphalt is placed in the Sunbelt states of Arizona, California, Florida and Texas. The Arizona DOT and local governments in Arizona primarily use asphalt rubber binder in open- and gap-graded hot-mixes to suppress highway noise.

Caltrans uses asphalt rubber in dense-, gap- and open-graded hot-mix asphalt, with local governments and Caltrans in southern California using asphalt rubber binders in gap- and open-graded mixtures. Texas DOT uses asphalt rubber primarily in gap-graded mixture, and Florida DOT uses a fine ground rubber at typically 6 to 12 percent by weight of asphalt binder in dense- and open-graded hot mixtures.

Highly Modified Asphalts

A new kind of SBS-modified asphalt binder – highly modified asphalt – now has been developed by Kraton Polymers.

In test applications in New England, north central states and in the southeast, the HiMA binder contained 7 to 8 percent SBS polymer, more than twice as much used in conventional polymer-modified binders as described above. Conventionally there has been a practical limit to polymer concentration; usually, as polymer concentration exceeds three percent, the viscosity of the binder increases such that the mix becomes more difficult to produce in the plant and less workable for the paving crew. The new HiMA polymer modifier is Kraton D0243, which gives workable mixes even at such high loadings. "We've adjusted the structure of the molecule so we retain the high temperature performance and elasticity characteristics of a conventional SBS modifier, but at the same time give it a much lower viscosity," says Kraton's Bob Kluttz. "The resulting HiMA binder yields an asphalt mixture with far greater rutting and fatigue resistance than conventional modified asphalt. This gives extended life, or even better, allows reduced pavement thickness for overall reduced cost." ❖