Chemistry and Microstructure of Polymer-Modified Coal Tar

By Steve Ratcliff and Frank O. Moore Jr.

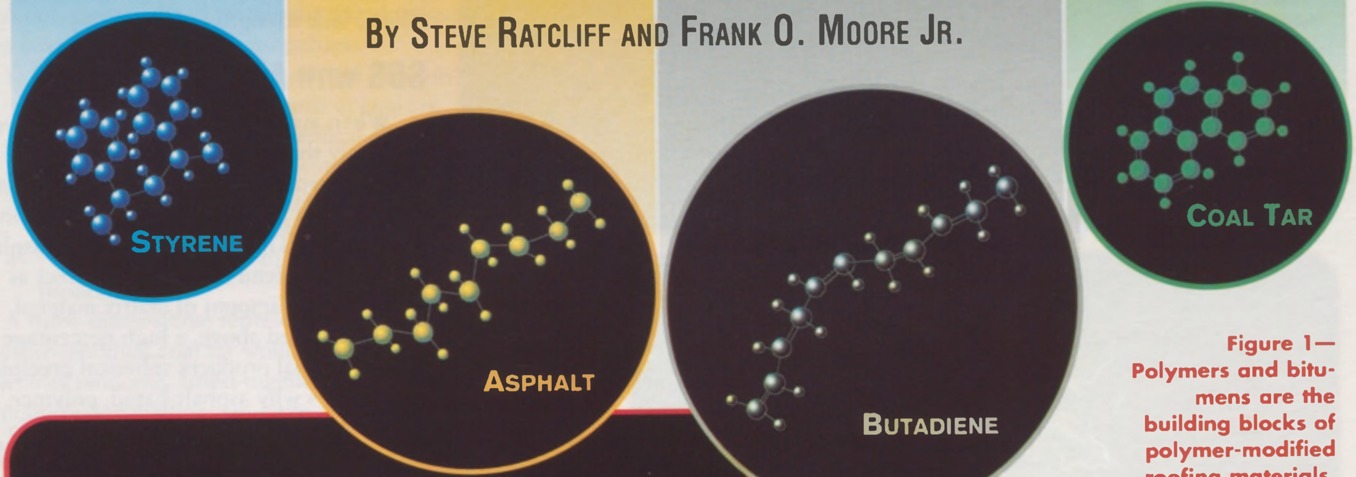

Figure 1—Polymers and bitumens are the building blocks of polymer-modified roofing materials. Shown here are the molecular structure of styrene and butadiene, which are the polymer compounds commonly used to modify asphalt.

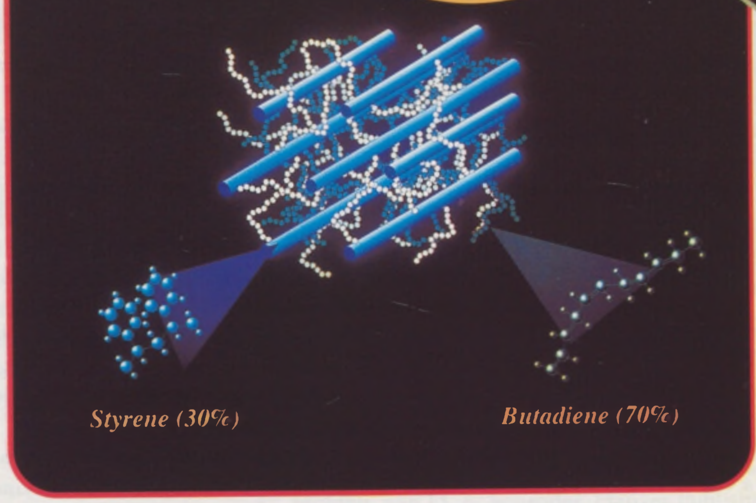

Figure 2—Artist's conception of the microstructure of SBS with no asphalt present. When the concentration of butadiene is much more than that of styrene, the styrene precipitates in a matrix of butadiene. The styrene forms spheres at low concentrations but forms cylinders as the concentration of styrene increases. If the concentration of styrene were much higher than the concentration of butadiene, then precipitates of butadiene would form in a styrene matrix.

Polymer modification is fascinating because it fundamentally alters material properties. Now, especially, this technology is of interest to the roofing community because there is a new polymer-enhanced bituminous roofing material available. Although research continues, there is enough now known to relate the chemistry and microstructure to the macroscopic properties.

Roof life cycles relate to chemistry. Unfortunately, nothing lasts forever, and even a perfectly installed roof will eventually deteriorate, due to the breakdown of its chemical components at the molecular level. The best that a roof owner can do is forestall these processes by choosing a roofing material with chemical attributes that contribute to a long-lasting, functioning membrane.

This paper presents simple models of the chemical components. Technical terms are avoided to stress the differences between the major classes of polymer-modified bitumens. In this simplified explanation, only four chemical components are mentioned, including two polymers and two bitumens (see *Figure 1*.) Using these building blocks, a graphical representation of polymer modified bitumens is presented. An attempt is made to relate the practical properties of the materials to the underlying chemistry and microstructure. First, the microstructure of polymer blends in the absence of any bitumen is described.

Polymer Components

The first two components can be called polymer A and polymer B. These building blocks can be part of the same molecular chain, with one of the polymers making up the ends. For example, in polymer-mod-

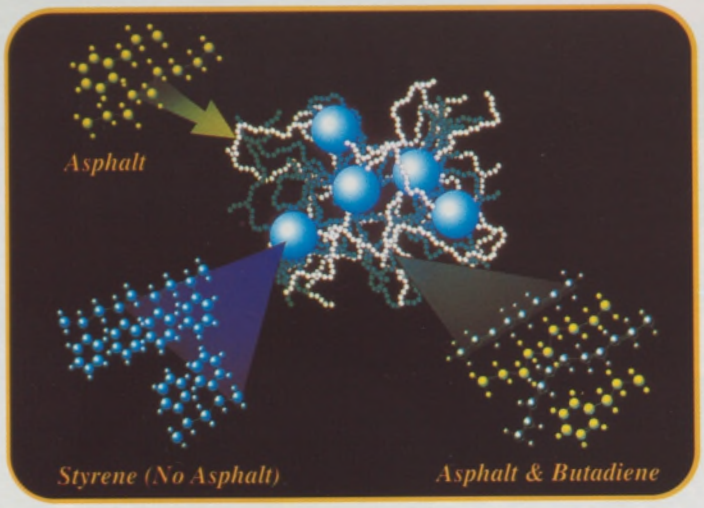

Figure 3— Asphalt won't dissolve in styrene. Absorption of asphalt by the butadiene matrix has the same effect as reducing the relative concentration of styrene. Thus, the styrene precipitates revert to a spherical shape.

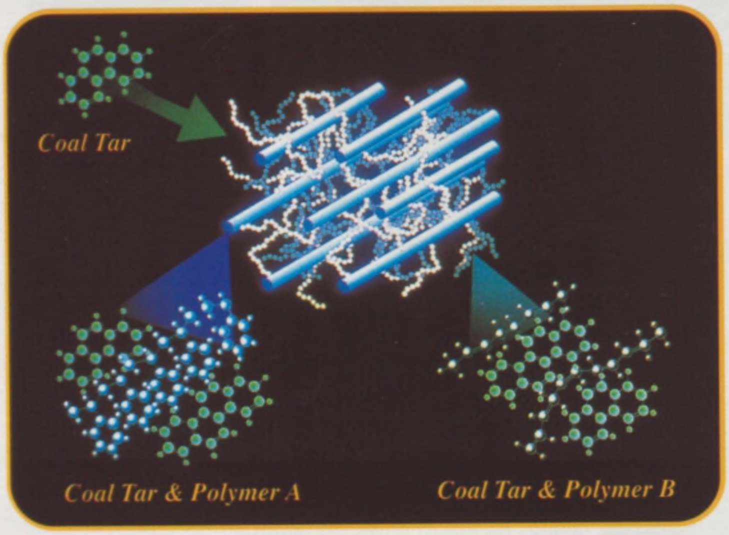

Figure 4— Coal tar is absorbed well by polymer A and B. Thus, the cylindrical microstructure of the polymer blend is retained. Also, the bitumen in this case becomes equally distributed throughout the material.

ified asphalt, the polymers typically are styrene and butadiene, and the copolymer is called styrene-butadiene-styrene (SBS), indicating that the styrene makes up the ends of the polymer chain. This structure has important consequences, imparting elastomeric properties to the blend. Chewing gum is unvulcanized styrene-butadiene rubber, while tires are made from a vulcanized styrene-butadiene rubber.

Depending on the relative proportions of the two polymers, one becomes the matrix, and the other becomes the precipitate. For example, in an SBS blend with a high concentration of butadiene, styrene precipitates in a matrix of butadiene (see *Figure* 2). The shape of the precipitate depends on the amount of precipitated material compared to the amount of matrix material. In pure SBS, spherical precipitates form at low concentrations of styrene, and cylindrical precipitates form as the concentration of styrene increases.[1]

The cylindrical microstructure can be seen in tiny samples examined under a transmission electron microscope. Slices through the cylinders appear as a hexagonal array of ellipses with similar orientation, revealing a microstructure of parallel cylinders.

The key to the elastomeric properties of SBS is that one polymer chain can terminate in different precipitates. Thus, the styrene precipitates pin the ends of long butadiene polymer chains, which can be curled up in the butadiene matrix. When the material is stretched, the chains straighten out, allowing the material to accommodate large strains; but the material returns to its original shape when the stress is removed.

This microstructure imparts strength and flexibility, which are desirable attributes in a roofing material. Bitumens such as coal tar pitch and asphalt provide waterproofing but (alone) lack strength and flexibility.

SBS WITH ASPHALT

When asphalt is blended with SBS, typically only the butadiene matrix becomes engorged with asphalt. Styrene is an aromatic compound and does not associate strongly with asphalt. Thus, the absorption of asphalt into the SBS blend has the same effect as increasing the amount of matrix material.

As discussed above, a high percentage of matrix material produces spherical precipitates. That's why asphalt-based, polymer-modified bituminous materials are said to have a spheroidal morphology. When SBS is added to asphalt, the shape of its precipitates remains spherical because the styrene absorbs very little, if any, of the asphalt.

Figure 3 illustrates how the asphalt is absorbed by butadiene but not by styrene. Although this microstructure can work as a roofing material, it is interesting to see what happens in the case of coal tar pitch.

POLYMER-MODIFIED COAL TAR PITCH

The breakthrough of the 1990s is the discovery that coal tar can be modified with polymers in a manner similar to asphalt. Polymer-modified asphalt has been used since the 1950s and is well established as a useful material for roofing systems. Polymer-modified coal tar can be understood using similar models. To avoid confusion, the polymers are designated as Polymer A and Polymer B.

An important difference is that coal tar is made up of aromatic organic compounds that mix well with other aromatic compounds. Using a proprietary technology, coal tar blends equally well with both polymers. Thus, both polymers benefit from the water-resistance and chemical resistance of the coal tar pitch. (see *Figure* 4.)

Furthermore, because both polymers become engorged with coal tar pitch, the relative proportion of the matrix material and the precipitate material is unchanged from the pure polymer blend. Thus, polymer-modified coal tar materials have the same cylindrical microstructure as the pure polymer blend (compare *Figures* 2 and 4.) That's what is referred to as the cylindrical morphology of polymer-modified coal tar. The cylindrical morphology can be verified under a transmission electron microscope.

Based on such macroscopic properties as cold-flex temperature and elongation, the cylindrical morphology appears to offer significant advantages over the spherical morphology. The extremely low cold-flex properties and stability of the compound may be due to the uniform distribution of coal tar through both polymer phases and the consistent particle size distribution. Because there is not a distinct boundary between the predominantly coal tar matrix and the predominately coal tar precipitates, the polymer-modified membrane behaves like a homogenous material. Internal boundaries can be the source of cracking and chemical deterioration, but in this material, the coal tar is present everywhere.

A polymer-modified membrane based on coal tar "inherits" from coal tar the following properties:

1) Resistance to attack by heat and photons because of the strong carbon-carbon bonds in coal tar.
2) Relative "immunity" to chemical attacks because the coal tar neutralizes reactive chemicals.
3) The chemical reactions that do occur yield by-products that are insoluble in water.
4) There is no tendency to crystallize or change physical properties.

A three-dimensional representation of the microstructure of polymer-modified coal tar would show knobby-shaped, aromatic molecules randomly fitted together in a tight, moisture-resistant, random (noncrystalline) structure, loosely interlaced with polymer chains. The long polymer chains are like a net that gives shape on the macroscopic scale. Yet the structure still is amorphous on the molecular scale, which is analogous to the contents of the net.

Other advantageous properties are present on the microscopic scale in the polymer-modified coal tar membranes. The polymers become engorged with aromatic coal tar molecules, which physically and chemically shield the polymers from the "forces of nature," including sunlight, oxygen, and water. Meanwhile, the polymers give the coal tar strength and flexibility. Normally, coal tar pitch becomes brittle at freezing temperatures, but when interlaced with polymer A and polymer B, its flexibility is extraordinary. The cylindrical microstructure of polymer-modified coal tar results in a low temperature flexibility lower than -55°C.

Science and Technology

The new materials are radically different from any other modified bitumen. They are as different from polymer-modified asphalt as coal tar pitch is different from asphalt. The aromatic compounds in coal tar are inherently more stable than the aliphatic compounds in asphalt. The carbon-to-carbon bonds are stronger for aromatics compared to the carbon-to-carbon bonds present in roofing asphalt.

When the polymers soak up many times their weight in coal tar pitch, they endow coal tar pitch with integrity, shape, and strength. This combination of strength, chemical stability, flexibility, and polymer structure is not found in any other bituminous roofing material.

Polymer modification of asphalt and coal tar membranes is now carried out in a manufacturing facility under controlled conditions. The resulting materials represent the fastest-growing segment of the roofing market.

Comparisons of bitumen-polymer blends suggest that the coal tar blends are unique. The graphic renditions presented here highlight the uniqueness of coal tar with polymer modification.

To summarize, blends of asphalt and polymers have a spheroidal microstructure in which asphalt is absorbed in the matrix and not in precipitates. The asphalt must be characterized to obtain a compatible blend; if the asphalt constituents are not balanced properly, then the resultant material will have properties that are unstable during weathering. In contrast, blends of coal tar with the polymers have a cylindrical microstructure where coal tar is absorbed by the matrix and precipitates. This structure results in a low temperature flexibility of - 55°C or lower.

Previously, modified bitumen membranes based on asphalt were the only choice available. Now coal tar polymer-modified bitumen membranes are also commercially available in a roll form—with low temperature flexibility, good weathering characteristics, excellent stability, and multiple application methods.

1. G. Holden and N. R. Legge, *Thermoplastic Elastomers Based on Polystyrene-Polybutadiene Block Copolymers, in Thermalplastic Elastomers—A Comprehensive Review*, ed. N. R. Legge, G. Holden, and H. E. Schroder, Hanzer Publishers, New York, 1987, pp. 50-61.

ABOUT THE AUTHORS

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