MODIFIED BITUMEN DURABILITY LINKED TO POLYMER PROTECTION

By Frank O. Moore, Jr.

Introduction

Modified bitumen membranes have gained a record of successful performance in the marketplace that can be attributed to the modification of the asphalt with polymers that enhance their physical properties. This enhancement of properties is carried out in the manufacturing facility under controlled conditions. Today, modified bitumens are a fast-growing segment of the roofing market. Materials with improved properties from polymer modification, including low temperature flexibility, good weathering characteristics, better temperature susceptibility, and a variety of application methods, are all desirable.

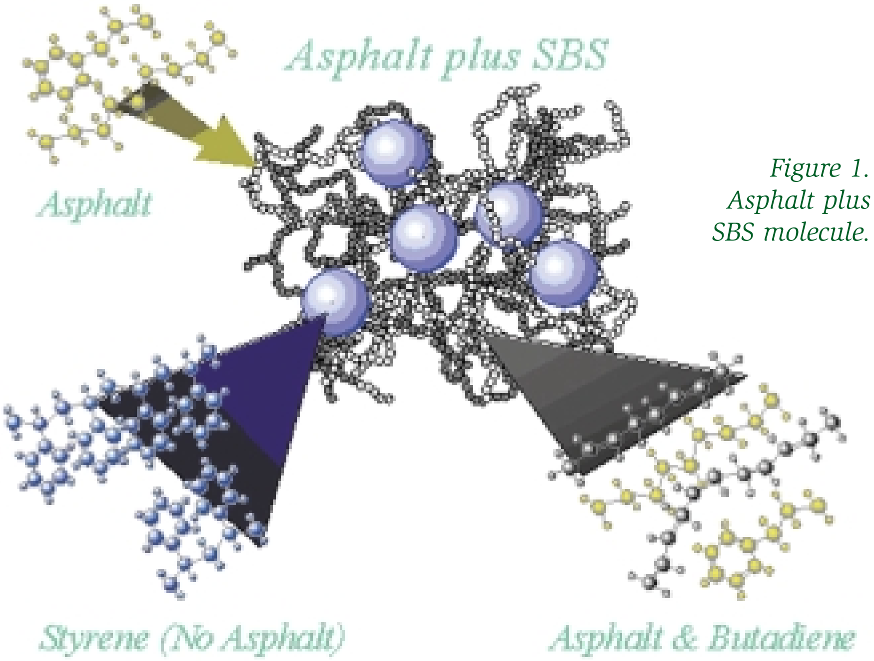

Figure 1. Asphalt plus SBS molecule.

The Modified Compound

Until recently, modified bitumen membranes utilizing asphalt were the only choice available. Honeywell International Inc. offers Millennium, a coal tar polymer modified bitumen membrane. Providing coal tar in a sheet form with polymer modification is unique. The uniqueness of the coal tar modified membrane is the polymer structure of the bitumen blend or compound as compared to asphalt bitumen blends.

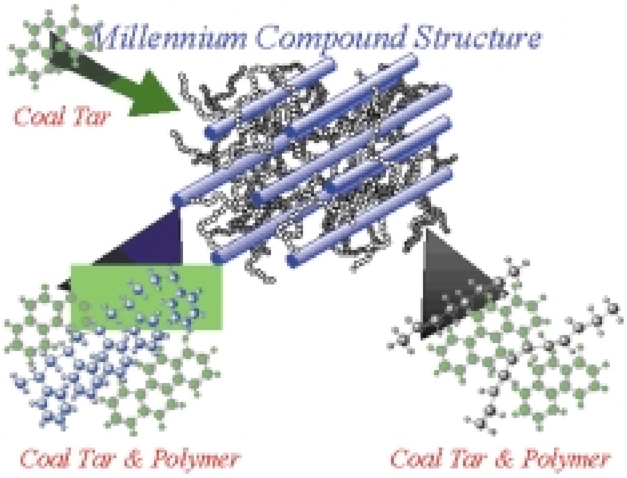

Figure 2. Millennium compound structure molecule.

The coal tar modified compound structure is cylindrical, indicating that the polymer absorbs the coal tar in both the butadiene and styrene domains of the polymer. This compound structure is due to the uniform distribution of the coal tar in both polymer phases, resulting in a product with a low temperature flexibility of -60˚C. The coal tar shield protects the polymer from the degenerative effects of sunlight, oxygen, etc., allowing the compound to retain physical properties imparted by the polymer, producing an extremely stable material.

Blends or compounds with asphalt and SBS-type polymers typically create a spherical polymer compound structure. This structure enables large amounts of the bitumen or asphalt to be absorbed into the butadiene with little absorption in the styrene polymer. Characterization of the asphalt used for polymer modification must be carried out and determined to have the proper constituents in the proper amounts to result in a compatible blend. If the balance of asphalt constituents is not as it should be, a material forms with properties that diminish quickly during weathering.

Protection of the polymer is of paramount importance, since the ability to protect the polymer from degradation will likely result in a compound capable of resisting the effects of aging due to exposure. This is illustrated by the lack of change in the low temperature flexibility, generally accepted as a physical property most affected by the aging and degradation of the polymer in modified bitumen sheets.

Accelerated Weathering

Degradation of the polymer in blends such as these can also be assessed by Gel Permeation Chromatography (GPC) identifying the cross-linking and chain scission that has occurred during exposure. G.W.J. Heimerikx and J.A.M. Van Hoek[1] utilized GPC to assess the typical condition of the polymer after exposure, along with the polymer-modified compound's cold bend properties.

Accelerated weathering of the coal tar, polymer-modified compound was carried out in accordance with ASTM D 4799, "Standard Test Method for Bituminous Materials (Fluorescent UV and Condensation Method)" in a horizontal (fluorescent UV and condensation) exposure machine. The specimens were exposed for 3,000 hours with half the specimen submerged in water. Thermal cycling was four hours UV exposure with 70˚C heat and four hours condensation with 40˚C heat. The specimens were removed from the exposure machine, tested for low temperature flexibility, and examined by transmission electron microscopy (TEM) to look for any change in compound structure. The membrane portion of the specimen submerged in water for 3,000 hours and the portion not submerged had the same low temperature flexibility (-60˚C) before and after exposure to the accelerated weathering. Further examination by TEM confirmed the blend to have the same properties as the material prior to being subjected to accelerated weathering.

Accelerated weathering of the coal tar modified bitumen and a commercially available asphalt modified bitumen was also carried out in accordance with ASTM D 4798, "Standard Test Method for Accelerated Weathering Test Conditions and Procedures for Bituminous Materials (Xenon-Arc Method)" utilizing specially-made quartz holders.[2] The quartz holders were used because it was determined they would not interrupt the radiance impacting the specimens and allowed half the specimen to remain submerged in water throughout exposure. These holders allowed water from the weatherometer spray to keep the bottom half of the holder full of water while subjecting the other portion of the specimen to alternate wetting and drying. Cycle A of ASTM D 4798 was utilized for the test conditions. This exposure is light only at 140 +/- 5˚F (60+/-3˚C) black panel temperature for 51 minutes and light with spray water at 45+/- 5˚F (7.2+/-3˚C) at the nozzle. This provides approximately a 100˚F change in temperature each hour of exposure.

Test Results

Specimens were exposed to these conditions for 6,000 hours and then examined. GPC was run on the compound of the specimens to determine the condition of the polymer.[3] Additionally, TEM was run on the samples to evaluate any change in the morphology of the compound. Low temperature flexibility was also performed on the exposed specimens. These tests were run on both the continuously

Figure 3. Horizontal (fluorescent UV and condensation) exposure machine.

Figure 4. Xenon Arc Machine.

submerged portion of the specimens and the portions subjected to the wetting and drying cycle.

The TEM revealed a hard-to-distinguish spherical morphology that is expected for SBS in asphalt. The fuzziness of the spherical domains appears to be from the degradation of the polymer. As the SBS polymer degrades and the asphalt hardens from exposure, some grafting between the components occurs, which can weaken the phase separation. The coal tar polymer modified compound, when examined by TEM, maintained its cylindrical morphology and all indications determined that it was as stable after exposure as prior to exposure. Morphologies of the specimens submerged in water and the portions subjected to wetting and drying were the same.

Low temperature flexibility was performed on all samples after exposure. The asphalt-modified compound lost 8.6˚C in low temperature flexibility. The coal tar polymer-modified compound had a -60˚C low temperature flexibility prior to exposure and -60˚C after exposure. The low temperature flexibility was the same for the portion of the specimens submerged in water and the portions subjected to the wetting and drying.

The GPC evaluated the condition of the polymer by determining the amount of crosslinking and chain scission that took place after exposure. A low level of chain scission can take place during processing and manufacturing (3-5%). The two samples of coal tar polymer-modified compound had 6-14% cross-linking and very low (7-9%) chain scission, while the asphalt-modified compound had 8-9% crosslinking and extensive chain scission. The chain scission of the asphalt compound was difficult to quantify because of the overlap in the SBS and asphalt peaks but was well over 50%. This condition was also observed in the above-cited reference. Again, there were no differences between the specimen portions submerged and the portions subjected to wetting and drying.

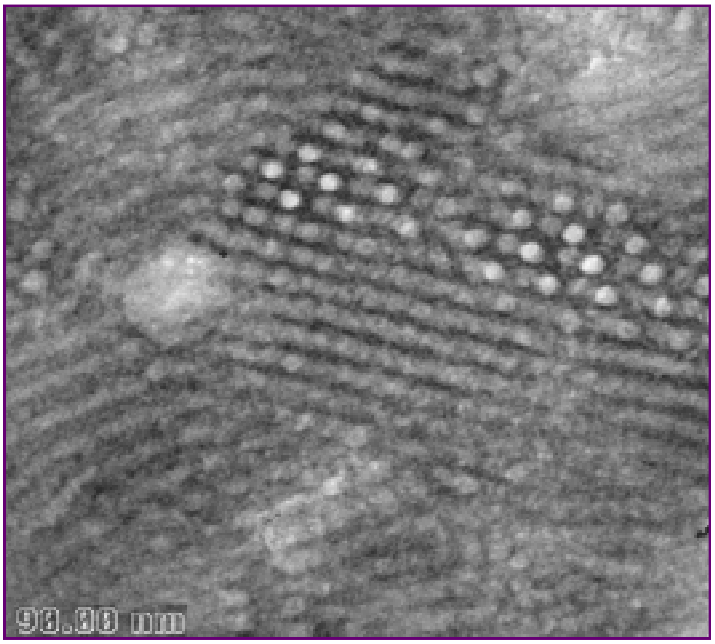

Figure 5. AS Millennium Gray - bottom

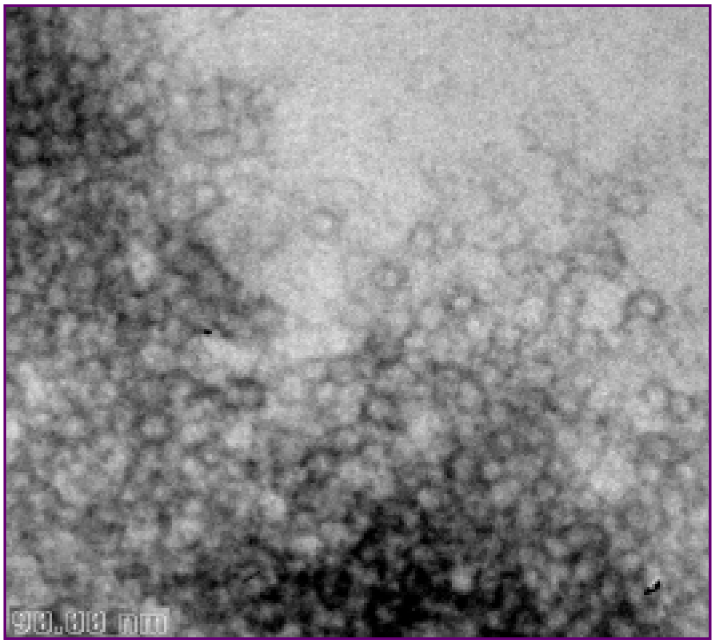

Figure 6. AS White Infinity - bottom

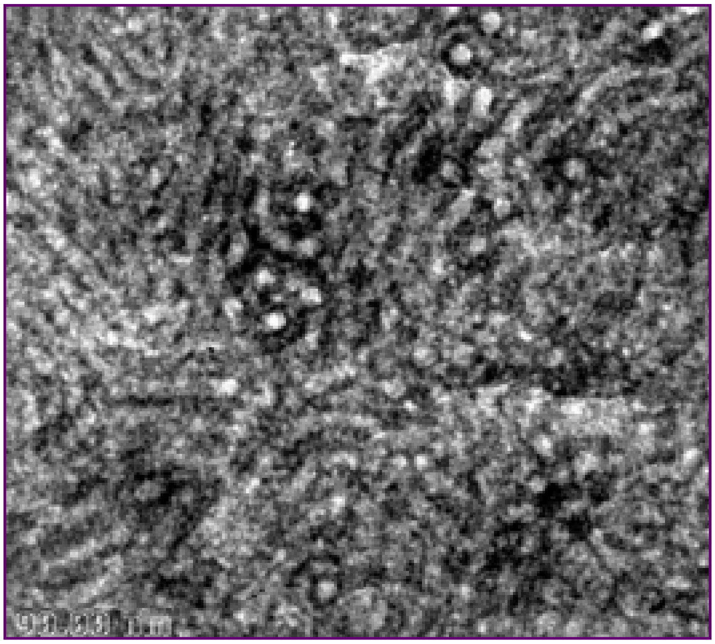

Figure 7. AS Millennium Gray - top.

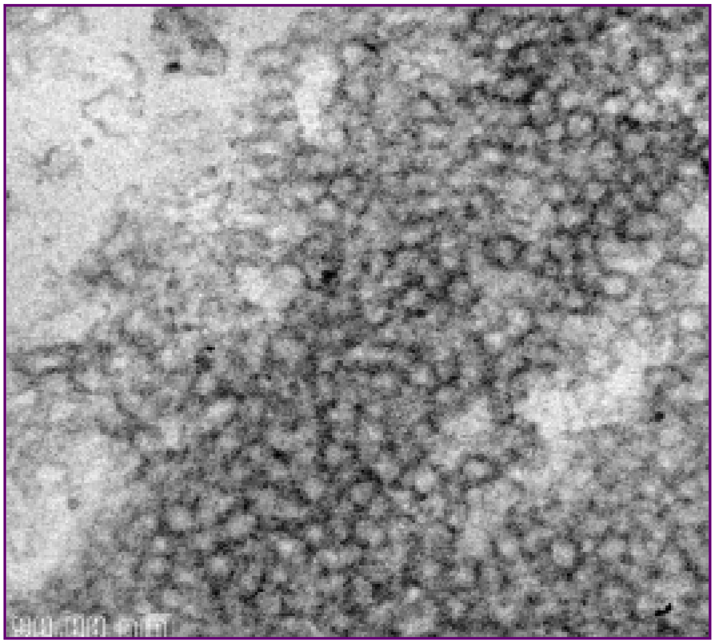

Figure 8. AS White Infinity - top.

Conclusion

One important item to note is that water does not appear to directly affect the degradation of the polymer. The oxidative degradation affected the asphalt-modified compound by age, hardening the asphalt with crosslinking and chain scission of the polymer, resulting from the asphalt's inability to protect the compound. In contrast, the coal tar polymer-modified compound had relatively no polymer degradation. Coal tar's inherent weathering properties, brought to the coal tar polymer-modified compound, provide the ability to prevent the oxidative effects of exposure from degrading the polymer, thereby allowing the compound to retain the same physical properties as before exposure. ■

Endnotes

1. Heimerikx, G.W.J., and Van Hoek, J.A.M., "A New Type of SBS Polymer with Improved Processibility and Durability (IPD)," *Proceedings of the Fourth International Symposium on Roofing Technology,* NRCA, 1997, p. 430.
2. Accelerated weathering and analysis were carried out at third party laboratories.
3. "Gel Permeation Chromatography" and Electron Microscopy analyses were conducted by KRATON Polymers U.S., LLC.

ABOUT THE AUTHOR

FRANK O. MOORE JR.

Frank O. Moore Jr. is Manager of Technical Services, Honeywell Inc. Commercial Roofing Systems. In his 30-year roofing industry career, Frank has held various technical positions in roofing materials manufacturing, product support, and product development. He has expertise in coal tar and asphalt built-up roofing and has worked on a polymer modification of asphalt and coal tar, including product development, technical support, and technical marketing. At Honeywell, Frank is responsible for the administration of all technical support, warranty programs, quality control, and specification processes. He resides in Clayton, NC, with his wife and son.