A NEW TYPE OF SBS POLYMER WITH IMPROVED PROCESSABILITY AND DURABILITY (IPD)

G. W. J. HEIMERIKX and A. J. A. M. VAN HOEK
Shell International Chemicals B.V.
Badhuisweg, Amsterdam, The Netherlands

The long-term performance of bituminous roofing sheets that are modified with styrene-butadiene block copolymers (SBC) is well-known and confirmed by the results of field studies on the performance of roofs existing throughout Europe. Nevertheless, a new class of polymers is being introduced, giving an improved durability in comparison to that of the standard SBS grades as demonstrated in laboratory tests.

The new polymers are based on styrene-butadiene-styrene block copolymers with a high-vinyl-content polybutadiene mid-block. The latter favors the maintenance under oxidative conditions of the load-bearing arms of the SBS polymer—which are important for the formation of the 3-D network—and promotes grafting reactions to bitumen components, both resulting in a better aging resistance. The high-vinyl-content polymers also give a more favorable (lower) high-temperature viscosity and, hence, may be exploited in optimizing the processing conditions during sheet manufacturing and/or in improving the durability.

KEYWORDS
High vinyl content, IPD polymers, roofing, SBC modified bitumen, SBS, SEBS.

INTRODUCTION

Long-term performance, or durability, is a main issue in the roofing industry for cost and guarantee aspects. Research and development, therefore, are focused not only on improving the initial properties of roofing sheet materials, but also on maintaining suitable properties over a longer period of service.

A field study recently carried out by Buro DakAdvies B.V. (BDA) on the long-term performance in service of 18 SBS modified bitumen roofs—with the age of the majority of the inspected roofs being 15 years and older—in various countries in Europe with different climatic conditions has shown their very good lifetime performance.1,2

Although the field study confirmed good aging resistance of SBC modified bitumens, questions continue to be raised whether further improvement can be obtained by using an SBC with hydrogenated mid-block (i.e., a styrene-ethylene-butylene-styrene [SEBS]) or by using special bitumens. The issue of further-improved SBC modified roofing sheets has been triggered, as well, by the application of polymer modified bitumen single-ply systems (i.e., systems with only one ply), which require high reliability. Hence, the aging characteristics of various types of SBC polymers in bitumen have been subject to investigation.

This paper highlights a new class of SBCs developed with the objective of further improving the aging characteristics and of preferably increasing the number of attractive processing performance properties during sheet manufacturing as compared to the commercial grades currently used.

To assess the durability of roofing sheets in outdoor service, a widely accepted laboratory aging test developed in past years was used. It is included in the “Special directives for the assessment of reinforced homogeneous waterproofing coverings of Styrene-Butadiene-Styrene (SBS) elastomer bitumen” according to the Union Européenne pour l’Agrément Technique dans la Construction (UEATC). Several properties of a sample before and after aging have to fulfill requirements in order to pass this test. Studies in France have revealed that passing this laboratory test is indicative of a service lifetime of about 20 to 25 years.4

THE DEVELOPMENT OF SBC POLYMERS WITH IMPROVED DURABILITY

In the past, the susceptibility of the SBC polymer unsaturated mid-block to aging resistance was the subject of studies. This particular aspect is one of the best documented parts in various studies and reports5,6 (“Vergelijking van SBS en APP gemodificeerde dakbedekking” includes a very extensive list of references). Atactic polypropylene (APP) as a modifier has also been included in these studies. These studies revealed that comparable aging resistance can be obtained from both APP and SBS modified bitumen membranes.

Regardless of the type of polymer, it is noted that a protective layer on a roofing sheet that is always recommended as the main part of the polymer modified compound is bitumen, which should be protected against aging (i.e., hardening). In this respect, the authors would also like to refer to the MRCA/NRCA APP and SBS Modified Bitumen Membrane Roofs: A Survey of Field Performance, which recommends protection for APP modified membranes.7

This paper will concentrate on the selection and the development of different types of SBCs, although it is known that the aging resistance of a polymer modified roofing compound can be influenced by the type of base bitumen, by the type of polymer, or by a combination of both.

Two different "penetration grade" base bitumens have been used for the bituminous blends: one 180 pen with an asphaltene content of about 11 percent (weight/weight)—which results in a distinct two-phase structure at high temperatures—and one with a low asphaltene content and a
fairly high aromaticity, which gives a single-phase blend. The two bitumens are often referred to as “incompatible” and “compatible,” although “less” and “more” compatible bitumens would be a more correct terminology. The softening point and the cold-bend performance of the systems based on compatible bitumen are generally slightly poorer and the viscosity somewhat higher than for the high-asphaltene-content blends. These poorer initial properties with a compatible base bitumen, however, are generally accompanied by a better aging resistance. These two bitumens are very suitable for model studies and, hence, were selected for the study.

SBC polymers that were subject of the study are commercially available SBS and SEBS polymers (SBC with a hydrogenated mid-block) and recently developed SBCs with a modified molecular design, which will be referred to as “a new class of polymers.”

**PERFORMANCE ASPECTS**

**SEBS Type of Polymers**

SEBS polymers are SBS polymers with a hydrogenated mid-block. Because of their saturated mid-block and, consequently, the absence of double bonds—which are susceptible to oxidation—SEBS-type of polymers show very good aging characteristics and high-temperature stability. Therefore, SEBS modification is suitable for use where very high application temperatures are required (e.g., in modified hot mopping bitumens).

However, the glass transition temperature \( T_g \) of the SEBS ethylene-butylene mid-block is about 30°C (54°F) higher than that of a comparable SBS butadiene mid-block (i.e., -60°C [-76°F] and -90°C [-130°F], respectively). This difference in \( T_g \) is reflected in the cold-bend temperature of the polymer modified bitumen, as shown in Table 1. This shows the results of blends of a linear, medium-molecular-weight, SEBS-type of polymer compared with a reference blend of a linear SBS with similar viscosity characteristics.

The aging characteristics of the blends were determined by the laboratory aging test according to the UEAtc, which involves the treatment of a sample in a dark, air-ventilated oven at 70°C (158°F) for six months.

Samples of the fresh material and of the material after six months of aging were tested on flow resistance and the cold bend. In absolute values, the difference between the cold-bend temperatures of fresh and aged samples of the SEBS/bitumen blend was smaller than that of the SBS/bitumen blend. It was clearly demonstrated that an SEBS-type of polymer is virtually not affected by the artificial aging at 70°C (158°F)—as assessed by Gel Permeation Chromatography (GPC)—and, hence, nearly the full effectiveness of the original SEBS content in the blend is maintained.

However, the initial cold-bend temperature of the fresh SEBS/bitumen blend was often insufficient to pass requirements for low-temperature flexibility for roofing sheet applications. This means that this SEBS/bitumen formulation has the better resistance to aging but also that the initial low-temperature flexibility performance is less than desired for roofs in colder climates.

**A NEW CLASS OF SBC POLYMERS**

It was found that SBS-type of polymers are vulnerable to a change in molecular structure caused by (artificial) aging, as was observed by a change in the GPC pattern of the area where the SBS peaks appeared (see Figure 1). The reduction of these peaks could be considered a loss of polymer caused by polymer breakdown. However, the performance properties after aging were much better than were expected on the basis of the reduction of the SBS peak in the GPC pattern.

The fact that the performance properties were retained is ascribed to a recombination of polymer segments and to the grafting of polymer segments on bitumen components, which is also indicated by the existence of products in a molecular weight range between that of the SBS and of the bitumen components. The loss in blend performance upon aging by the reduction of effective SBS is largely compensated for by these recombination and/or grafting reactions with the overall result that the properties are, to a great extent, retained. This recombination of polymer segments and grafting to bitumen was not observed for SEBS systems (see Figure 2).

Essential for the properties of an SBC modified bitumen is the existence of the three-dimensional network and its maintenance during service life. Oxidation of the double bonds in the polybutadiene mid-block leads, for example, to polymer fragments consisting of a polystyrene end-block with a polybutadiene tail. These species still form (polystyrene) domains, but do not contribute in the 3-D network because the load-bearing arm (polystyrene-polybutadiene-polystyrene) does not exist anymore.

Therefore, efforts were focused on the development of a polymer with a polybutadiene mid-block—favoring a good low-temperature flexibility and recombination/grafting reactions—but with a better retention of the 3-D network. The answer was found in high-vinyl-content SBCs.

In the currently used anionic polymerization of 1,3 butadiene, mainly 1,4 addition takes place. However, with the use of modifiers, a 1,2 addition can be promoted, resulting in a polybutadiene mid-block with an increased vinyl content.

The benefits of high-vinyl-content polymers toward aging resistance are twofold:

- a higher reactivity towards oxidation of the vinyl double bond compared to that of the polybutadiene double bond
- higher reactivity of the vinyl group favoring grafting reactions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>SBS</th>
<th>SEBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg mid-block (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Softening point, R&amp;B (°C)</td>
<td>103</td>
<td>106</td>
</tr>
<tr>
<td>Viscosity, at 180°C at shear rate 103s⁻¹ (Pa.s)</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Cold Bend, pass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh (°C)</td>
<td>-35</td>
<td>-10</td>
</tr>
<tr>
<td>Aged at 70°C for 6 months (°C)</td>
<td>-20</td>
<td>-5</td>
</tr>
<tr>
<td>Flow, pass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh (°C)</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Aged at 70°C for 6 months (°C)</td>
<td>65</td>
<td>105</td>
</tr>
</tbody>
</table>

*Table 1. Performance properties of blends of 12 percent polymer (SBS vs. SEBS) in a compatible base bitumen.*
The former will lead to a preferential oxidation of the vinyl double bond, which will affect the overall molecular weight to a limited extent only but will leave the load-bearing arm intact. Even after oxidation of these double bonds, the 3-D network will be maintained.

The higher reactivity of the vinyl group will further favor grafting reactions, which have been proven to represent an important contribution in retaining properties upon aging.

A drawback from an increase of the vinyl content is an increase of the $T_g$ of the polybutadiene mid-block. The con-
relation between the vinyl content and the $T_g$ of the butadiene rubbers has been described by the following (Fox) equation:

$$\frac{1}{T_g} = \text{vinyl}\% / T_g(100\% \text{ vinyl}) + (1-\text{vinyl}\%) / T_g(0\% \text{ vinyl})$$

with $T_g(100\% \text{ vinyl})=261$ K and $T_g(0\% \text{ vinyl})=170$ K

An increasing vinyl content will, thus, result in a higher (poorer) $T_g$ of the mid-block (see Figure 3) and, hence, a higher (poorer) cold-bend temperature. The results of the cold-bend temperatures according to the UEAtc, which are presented in Figure 3, clearly demonstrate this effect. It should be realized that this test is carried out with temperature increments of 5°C (9°F), which means that gradual changes will not be found.

There is a known correlation between the molecular weight and the high-temperature viscosity for SBCs with polybutadiene mid-blocks that contain, in general, a low amount of vinyl groups.

When the vinyl content increases at constant molecular weight, the inherent viscosity of the mid-block decreases because of the shorter backbone chain. Also, the thermal-dynamic incompatibility between the styrene blocks and the mid-block increases. The first effect leads to a decreased polymer viscosity of the high-vinyl mid-block SBS, whereas the latter effect has an opposite sign. As the magnitude of both effects cannot be assessed theoretically, this had to be verified. It was found that at a same molecular weight, the viscosity is lower with the high-vinyl-content polymers in comparison to that of the standard SBC polymers.

The performance properties and aging characteristics of the newly developed SBCs have been assessed on blends of 12 percent polymer in a 200 pen compatible bitumen, as well as in a 180 pen incompatible base bitumen. Table 2 reports the results obtained of blends of one specific radial, high-molecular-weight, new type of SBC polymer (IPD-1) with reference blends of a radial SBS as commonly used in the roofing industry.

The results show that with the new polymer (IPD-1), the performance-related initial properties are rather similar to those of the conventional SBS: a slightly better flow resistance and a somewhat poorer low-temperature flexibility that is, however, sufficient to pass UEAtc requirements on initial properties. The advantage of the new polymer over the conventional polymer is a reduction of the high-temperature viscosity by about 40 percent. This significant influence on the viscosity—which is an important production parameter—enables the manufacturers to reduce costs and/or to increase production rates:

- Manufacturing of roofing sheets on the basis of IPD-1 modified bitumen at the same viscosity level of that on the reference SBS-based blends allows:
  - A lower coating-bath temperature, which results in energy savings. Next to this, the lower coating-bath temperature will allow less elongation of the carrier and, hence, will result in a better quality product.
  - A higher filler content, which reduces production costs.

- Manufacturing of roofing sheets on the basis of IPD-1 modified bitumen at a lower viscosity level than that on the basis of the reference SBS blends allows a higher line speed and, hence, a higher production rate.

From the results before and after aging, it is concluded that these new polymers exhibit an improved aging resistance (i.e., better maintenance of the flow resistance and the cold-bend performance under aging conditions, as compared with commercially available SBS polymers.)

The potential of this new class of polymers is visualized in a polygon. Performance-related properties of fresh materials, such as softening point; flow resistance temperature; cold-bend temperature; service temperature range (STR), the difference between the flow and cold-bend temperature; and the high-temperature viscosity at 180°C (356°F), are shown together with the changes as a result of aging expressed as the difference in softening point, cold-bend temperature, and the service temperature. The values at the axes have been set in such a way that a better performance is represented by a larger polygon. This presentation of the properties gives a quick and complete insight in the potential advantages of the new polymer.

In Figures 4 and 5, examples of the performance possibilities of this new class of polymers are given. Figure 4 represents polymer IPD-1, which gives performance properties close to those of the commercial available SBS, but with a reduced high-temperature viscosity and improved aging characteristics. Figure 5 shows a new polymer, IPD-2, that was designed to obtain a significantly improved flow resistance temperature in combination with a better aging resistance at
Figure 4. “Polygon” of new polymer IPD-1 and reference SBS in blends with compatible bitumens.

Figure 5. “Polygon” of new polymer IPD-2 and reference SBS in blends with compatible bitumens.

an acceptable low viscosity level. The latter polymer is seen to fulfill the requirements in warm(er) climatic areas.

CONCLUSIONS

SBC polymers in blends with bitumen for roofing applications exhibit excellent performance properties and high durability in the laboratory, as well as in field studies. Through special molecular design, further improvement on the durability and processing characteristics has shown to be possible:

- The new high-vinyl-content SBC polymers blended with bitumen result in an excellent combination of performance properties with a reduced high-temperature viscosity, being advantageous for roofing sheet manufacturing economics.
- The new high-vinyl-content SBC polymers (IPD polymers) have been shown to provide in bitumen improved aging resistance, which may be exploited to improve durability.

REFERENCES


7. APP and SBS Modified Bitumen Membrane Roofs: A Survey of Field Performance, the Midwest Roofing Contractors Association and the National Roofing Contractors Association, 1996.