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Rheology of Iraqi Asphalt Modified with SBS, Polyphosphoric Acid and Sulfur

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Abstract: Polymer modified asphalts (PMA) became of great interest over the last years because there are closely related to industrial and constructional fields. To increase the elasticity of asphalt, styrene-butadiene-styrene (SBS) type polymers are used which are elastomeric block copolymers. Although the addition of SBS type block copolymers has economic limits and can show serious technical limitations, it is probably the most appropriate polymer for asphalt modification. The present work seeks to identify the changes on the rheological and physical properties of SBS modified with Dora asphalt. So it is the first study using Iraqi asphalt with styrene-butadiene-styrene. In this paper polyphosphoric acid PPA and sulfur were used to improve the high temperature property and storage stability of SBS modified asphalt.PPA can improve the high temperature performance of the SBS modified Dura asphalt evidently but declain the storage stability. Owing to the gelation of PPA, the phase separation of SBS becomes more serious.

Keyword: Polyphosphoric acid, Sulfur

Introduction

The use of styrene-butadiene-styrene triblock copolymer (SBS) as an asphalt modifier was developed by the Shell Chemical Company (Holden et al., 1969). It has been recognized that the physical and mechanical properties and rheological behavior of conventional asphalt compositions can be improved by the addition of SBS (Lu, 1997). SBS exhibits a two-phase morphology consisting of glassy polystyrene (PS) domains connected together by the rubber polybutadiene (PB) segments at the temperature s between glass transition temperatures of the PB and PS, so SBS exhibits crosslinked elastomer network behavior. Above the glass transition temperature of PS, the PS domains soften and SBS becomes melt process able. This behavior of a thermoplastic elastomer has allowed SBS to become one of the promising candidates in asphalt modification (Shuler et al., 1987). However, because of the poor compatibility between SBS and asphalt, the storage stability of SBS-modified asphalt is usually poor at elevated temperature, which is the major obstacle to the application of SBS-modified asphalts in paving (Wang et al., 2003). PPA and sulfur as the major modifiers in improving the high temperature performance or storage stability of SBS modified asphalt have been used widely in practice. PPA as an important asphalt modifier can improve the hightemperature property of asphalt greatly due to the gelation effect. It is also reported in some publications that the storage stability of PMAs can be improved by the addition of PPA (Welborn , 1983; Babashak, 2005; Maldonado, 2005), however this conclusion is still in question.

Literature Review

The chemical complexity of an asphalt binder precludes any precise molecular identification (Masson, 2008). This formulates the approach of analyzing asphalt binders based on families of compounds. These families are termed as Saturates (S), Aromatics (A), Resins (R), and Asphaltenes (As), which are often called as the SARA fractions. The molecular weights of SARAs vary between 300 and 1000 Daltons (Peramanu, 1999). As stated by Lesueur (Lesueur, 2009), ‘‘Bitumen must be thought of as a chemical continuum with gradual increase of molar

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mass, aromatic content and polarity from saturates to asphaltenes." The SARA fractions keep on forming larger molecules through associations. Saturates are wax-like simple aliphatic chain compounds. The SARA fractions increase the aromaticity and heteroatomic contents in the order S < A < R < As (Speight, 2014). The Aromatics and saturates serve as the continuous phase while the Asphaltenes remain as the dispersed phase stabilized by the Resins in the continuous matrix. The dispersion was addressed by a colloidal bitumen model proposed by Pfeiffer (Pfeiffer, 1940). According to the colloidal model, the Asphaltenes are the solid phase remaining dispersed in the maltenes.

Asphalt binders are often modified by PPA to improve their performance. The performance grade (PG) system requires expanding the useful temperature interval (UTI) for binders those are required to be used in high pavement temperature regions. According to a recent study (Baumgardner, 2005), achieving the UTI greater than 92 C requires some sort of modification to the neat (unmodified) binder. The PPA is an oligomer of H_3PO_4, which is obtained through dehydration of H_3PO_4 at high temperatures or by heating P_2O_5 dispersed in H_3PO_4 (Jameson, 1959). A number of possible reactions between PPA and asphalts obviously exist where no single reaction is satisfactory by itself (Baumgardner, 2005). The reaction is primarily dependent on the base asphalt. PPA reacts with the asphalt binder through phosphorylation(Orange et al., 2004) . However, PPA helps elevate the higher temperature grade, and thus the rheological properties without affecting the low temperature properties (Baumgardner, 2005).

Materials and Experimental

The materials used in this study are:

Asphalt:

One type of asphalt binder was used in this study, it is (40-50) penetration grade from Dura Refinery. The physical properties of asphalt before add SBS that used are tabulated in Table (1).

Table 1.Physical properties of asphalt before add SBS

General physical properties	The value in modified
Specific Gravity @ 15.6^{o}C	1.04
Flash point ^{o}C	326
Ductility @ 25 ^{o}C (cm)	100+
% wt. Solubility. in CH_2CL_3	99.9
Penetration. @25 ^{o}C (100gm,5sec. 0.1 mm)	40
Original of penetration After loss on heat %	92
Softening point ^{o}C	51.5
H_2O % Vol	NIL

SBS:

Styrene-Butadiene-Styrene polymer (SBS) D1192 in the form of porous pellet were obtained from Kraton polymers(USA). As show in figure (1).

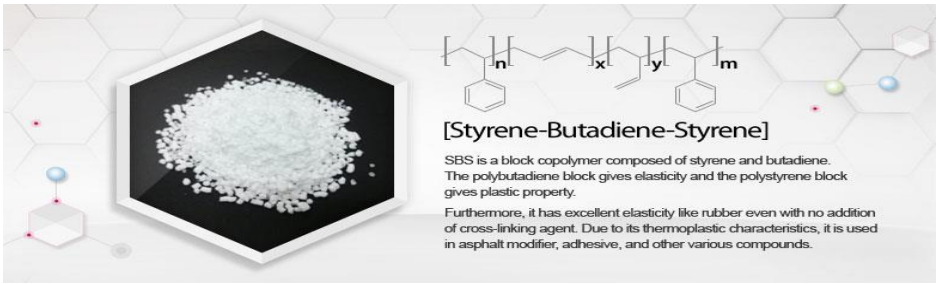

Figure 1. Chemical formula SBS

Preparation of Samples

To prepare polymer modified asphalt blends,100gm of the base asphalt was placed into a 1L metal container and heated to fluidity. After that, the fluid asphalt was mixed with SBS & additive using a mechanical stirrer 160-165^{o}C for about 5h, as shown in Table (2)

Table 2.The proportion of SBS modified asphalt

	1192	1192/ PPA		1192 / sulfur	
Polymer content	1	1	2	1	2
Sulfur content	0	0	0	0.5	0.5
PPA content	0	0.1	0.1	0	0

1192: The SBS modified asphalt
1192/PPA: The SBS 1192/PPA compound modified asphalt.
1192/sulfur: The SBS 1192 / sulfur compound modified asphalt.

SARA Analysis

The SARA analysis was performed in accordance with ‘‘ASTM D 4124-09: Standard Test Method of Separating Asphalt into Four Fractions” (ASTM D 4124-09).

Conventional Test

Softening point test (ASTM D 36, 2009),Penetration test (ASTM D 5, 2006) and ductility test (ASTM D 113, 2007) (ASTM D 36, 2007, ASTM D 36, 2009, ASTM D 36, 2006)

Results and Discussions

Asphalt can be divided into four parts, as show in the Table (3) which shows that the of asphaltene ratio represents 19% of the overall asphalt composition. the separated maltenes by a chromatography column, shared that asphalt was found to be rich with aromatic compounds compared to saturated compounds, as described in Table (3):

Table 3. The contents and appearances of SARA fractions in asphalt

SARA fraction	Content (wt%)	Appearance
Saturates	19.53%	Colorless or Yellow Oil
Aromatics	26.80%	Yellow or red sticky liquid
Resins	29.47%	Brown viscous semi-solid
Asphaltenes	19%	Black fragile powder solid

Physical Measured

As is seen in Table (4) the addition of SBS in the range of 1 wt%, 2 wt% into pure asphalt decreased penetration while ductility continued at the same level,, the accrual of SBS in asphalt led to increase the softening point in modified binders. The decline in penetration with the increase of the softening point signaled a significant increase in hardness of the bitumen, and a decrease in its temperature susceptibility

Table 4.The physical properties of the SBS1192- modified asphalt

	1192	1192/ PPA		1192 / sulfur	
Softening point (ºC)	56	59	60	54	60
Penetration (25 ºC, dmm, 0.1 mm)	22	21	19	31	25
Ductility (25 ºC, cm)	100+	+100	+100	100+	+100

Conclusions

In this study the impact of SBS additive to performance properties of bitumen was investigated: The results of the conventional tests signify that an increase in the stiffness of bitumens with the addition of SBS Polymer into pure bitumen, and a decrease in temperature susceptibilities of bitumen take place. This indicates that SBS modified binders can especially be used at the regions with high temperatures.

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