ABSTRACT

The present invention provides a modified asphalt composition showing excellent ductility and thermal stability at low temperature and the resistance to permanent deformation at high temperature comprising i) 100 wt. part of natural asphalt; and ii) 0.5–40 wt. part of asymmetric styrene-butadiene-styrene triblock copolymer having number average molecular weight of 20,000–1,000,000. Modified asphalt composition of present invention can be used for pavement of road or manufacturing water proof sheet.
ASPHALT COMPOSITION CONTAINING STYRENE-BUTADIENE-STYRENE BLOCK COPOLYMER HAVING ASYMMETRIC POLYSTYRENE BLOCK

FIELD OF THE INVENTION

[0001] The present invention relates to a modified asphalt composition containing asymmetric styrene-butadiene-styrene triblock copolymer as modifier. More particularly, this invention relates to a modified asphalt composition containing asymmetric styrene-butadiene-styrene triblock copolymer showing an excellent balance of ductility at low temperatures and high flow resistance at high temperatures.

BACKGROUND OF THE INVENTION

[0002] Conventional bitumen asphalt compositions frequently can not meet all of the requirements, when it is used for pavement of road or manufacturing water-proof sheet. Further, at high temperature, the permanent deformation of asphalt composition can occur due to high temperature and high pressure. Also, at low temperature, the fatigue crack can occur at the bottom of asphalt by repeated weight pressure whereas the cracking can occur at the top of asphalt by repeated tensile strength according to rapid change of temperature. Further, a natural asphalt composition has the drawbacks by declining the resistance against permanent deformation, thermal sensitivity, fatigue crack and/or low temperature crack according to the lapse of time and increase of vehicles after pavement of road.

[0003] To solve above problems, a modified asphalt composition has been developed by addition of polymer to the asphalt. For example, low density polyethylene, ethylene vinyl acetate, styrene-butadiene rubber, butyl rubber and/or mixture of them have been used for asphalt modifier to resist the permanent deformation at high temperature as well as to resist impact crack caused by repeated weight pressure and tensile strength at low temperature. Of course, the application of modified asphalt has been increasing in the field of industry.

[0004] In U.S. Pat. No. 3,985,694 (Richard J. Petrucco et al) and U.S. Pat. No. 4,130,516 (Duane W. Gagie et al), a modified asphalt composition has been disclosed by addition of thermoplastic elastomer, such as, linear polyethylene, ethylene vinyl acetate and/or styrene-butadiene rubber to the asphalt.

[0005] In U.S. Pat. No. 3,345,316, an asphalt composition comprising polychlorophenylene resin, 10–30 wt. part of thermoplastic elastomer, such as, linear styrene-butadiene-styrene triblock copolymer or styrene-ethylene-butylene-styrene block copolymer without addition of sulfur has been disclosed. Further, economical manufacturing process and excellent compatibility of this composition have been suggested as the merits of this composition.

[0006] Further, a radial type of styrene-butadiene block copolymer has been also suggested as asphalt modifier, because it enhances the processibility, softening point, stability and/or viscosity of asphalt composition. Such asphalt composition can be used as looping, coating, hot-melt, asphalt concrete and/or silant composition.

[0007] On the other hand, in U.S. Pat. No. 4,130,516, an asphalt composition comprising asphalt, sulfur and/or polymer has been disclosed. The polymer can be a natural rubber or a synthetic rubber. The enhancement of ductility can be accomplished by application of linear styrene-butadiene random copolymer, whereas there is no enhancement of ductility by application of radial styrene-butadiene random copolymer.

[0008] In U.S. Pat. No. 5,130,354, an asphalt-diene polymer composition with improved adhesion to polar materials has been disclosed. In this disclosure, a silane functionalized polymer of conjugated diolenin wherein silane functionality is grafted onto the polymer has been disclosed. Further, in U.S. Pat. No. 4,443,570, styrene-ethylene-butylene-styrene block copolymer saturated with hydrogen has been used as asphalt modifier. The softening point of asphalt composition comprising asphalt, organic solvent, silica and styrene-ethylene-butylene-styrene block copolymer can be adjusted around at 140°F.

[0009] On the other hand, in U.S. Pat. No. 4,412,019, an asphalt composition comprising asphalt, sulfur and styrene-ethylene-butylene-styrene block copolymer has been disclosed. In this disclosure, it has been reported that the ductility and tensile strength at low temperature can be enhanced by the increase of the amount of asphalt modifier.

[0010] Further, in Korean laying open patent publication No. 2002-13709, the mixture of linear styrene-butadiene-styrene triblock copolymer and radial styrene-butadiene block copolymer has been suggested as asphalt modifier. In this disclosure, the addition of mixture of 40–100 wt. part of linear styrene-butadiene-styrene triblock copolymer and 60–0 wt. part of radial styrene-butadiene block copolymer to the asphalt has showed excellent and balanced physical properties of asphalt, such as, solubility, high temperature storage stability, good ductility and good tensile strength, good adhesion and good softening point.

[0011] As described above, it has been known that a modified asphalt composition shows excellent physical properties, such as, good thermal resistance, anti-aging property and resistance against permanent deformation. Such enhancement of physical properties in modified asphalt composition results from the increase of liquidity resistance caused by high viscosity at high temperature, the increase of impact resistance at low temperature and the increase of anti-aging property from light or air, because the polymers in asphalt composition enhances the matrix of asphalt by forming polymer domain.

[0012] However, the anti-crack property at low temperature depends on the ductility of asphalt composition. If the ductility of asphalt composition increases, the liquidity of modified asphalt composition is enhanced at low temperature. Of course, the crack of asphalt caused by pressure fatigue or thermal deformation is also declined if the ductility of asphalt composition increases. Therefore, ductility is very important factor for estimating the crack resistance at low temperature.

[0013] On the other hand, in the case of water-proof sheet, the deformation caused by crack in low temperature can be protected by addition of polymer. To evaluate the characteristics of property in low temperature, ductility has been regarded as major estimation factor.

[0014] Generally, asphalt polymer modifier has a role for enhancing liquidity and declining the thermal sensitivity in
low temperature as well as for resisting the deformation in high temperature. Further, it has a role for improving physical properties, such as, tensile strength, stiffness, tenesity, adhesion with aggregate.

[0015] On the other hand, the improvement of stability in low temperature depends on the kinds of polymers inserted as modifier. Even though the structure of polymer is similar, the resistance against thermal sensitivity can be varied.

[0016] Conventionally, polyolefin, styrene-butadiene random copolymer rubber and/or styrene-butadiene block copolymer rubber can be used as asphalt modifier. Especially, it has been known that styrene-butadiene random copolymer rubber or styrene-butadiene block copolymer rubber has a role for enhancing ductility, which prevents the crack caused by repeated tensile force at low temperature.

[0017] On the other hand, a modified asphalt composition containing the wasted tire powdered at extremely low temperature has been suggested. However, despite of economical advantage, the physical properties for asphalt modifier is less than those of styrene-butadiene block copolymer rubber. Further, ethylene-propylene diene monomer rubber can be used as asphalt modifier. However, the application of this modifier has to be restricted due to its high melting point and high cost.

[0018] On the other hand, to prevent phase separation between asphalt and polymer modifier, amine compound, sulfur compound and/or polymer substituted with polar radical group have been generally used.

[0019] The inventors of present invention have researched an enhanced asphalt modifier showing excellent ductility at low temperature, while the physical properties in high temperature have been still maintained. We have found that asymmetric styrene-butadiene-styrene block copolymer enhances the ductility and thermal stability of asphalt composition at low temperature, which has not been anticipated from conventional asphalt modifier, such as, linear or radial styrene-butadiene block copolymer rubber.

**SUMMARY OF THE INVENTION**

[0020] The object of the present invention is to provide a modified asphalt composition containing asymmetric styrene-butadiene-styrene triblock copolymer as modifier showing excellent ductility and thermal stability at low temperature and the resistance to permanent deformation at high temperature.

[0021] Further, the object of the present invention is to provide a modified asphalt composition comprising i) 100 wt. % part of natural asphalt; and ii) 0.5–40 wt. % part of asymmetric triblock copolymer having number average molecular weight of 20,000–1,000,000 represented as following formula 1.

\[
A-B-A' \quad \text{(formula 1)}
\]

[0022] wherein

[0023] A represents a vinyl aromatic polymer block having number average molecular weight of 8,000–30,000;

[0024] B represents a conjugated-diene polymer block or a conjugated-diene copolymer block having a small amount of vinyl aromatic monomers; and

[0025] A' represents a vinyl aromatic polymer block having number average molecular weight of 500–5,000;

[0026] wherein the weight amount of A and A' block is 5–40 wt % of total A-B-A' triblock copolymer, and the percentage of vinyl aromatic monomer in the block A-A' as to total vinyl aromatic monomer amount in A-B-A' is 50–98%.

[0027] Further, said vinyl aromatic polymer block (A or A') comprises monomers at least one selected from the group consisting of styrene, α-methylstyrene, o-methylstyrene, p-methylstyrene and p-tert-butylstrene; and said vinyl aromatic monomer is preferably a styrene.

[0028] On the other hand, said conjugated-diene polymer block (B) is a homopolymer block consisting of butadiene or a tapered block consisting of most of butadienes and a small amount of conjugated diene monomers.

[0029] Further, the number average molecular weight of said compound of formula 1 is 50,000–400,000.

[0030] Further, the asphalt composition preferably comprises i) 100 wt. % part of natural asphalt and ii) 1–20 wt. % part of asymmetric triblock copolymer represented by formula 1.

[0031] On the other hand, the present invention also provide a modified asphalt composition further comprising linear or radial block copolymer as to the modified asphalt composition described above.

[0032] Further, the present invention also provide a usage of said modified asphalt composition as to pavement of road or manufacturing water proof sheet.

**DETAILED DESCRIPTION OF THE INVENTION**

[0033] The present invention can be described in detail as follows.

[0034] The asphalt modifier of the present invention can be an asymmetric styrene-butadiene-styrene block copolymer represented by formula 1. The number average molecular weight of asymmetric styrene-butadiene-styrene block copolymer represented by formula 1 is 20,000–1,000,000, preferably 50,000–400,000.

[0035] If the number average molecular weight of said block copolymer is less than 20,000, the mechanical properties of copolymer can not be fully expressed. On the other hand, if the number average molecular weight is more than 1,000,000, the processibility of copolymer can be declined.

[0036] Said vinyl aromatic polymer block (A or A') comprises monomers at least one selected from the group consisting of styrene, α-methylstyrene, o-methylstyrene, p-methylstyrene and p-tert-butylstrene, and said vinyl aromatic monomer is preferably a styrene. Further, the weight amount of A and A' block is 5–40 wt % of total A-B-A' triblock copolymer, and the percentage of vinyl aromatic monomer in the blocks A-A' as to total vinyl aromatic monomer amount in A-B-A' is 50–98%.

[0037] The difference of number average molecular weight between block A and block A' can be 3,000–20,500, which shows that block A and block A' are asymmetric blocks.
[0038] Said conjugated-diene polymer block (B) is a homopolymer block consisting of butadiene or a tapered block consisting of most amount of butadienes and a small amount of conjugated diene monomers.

[0039] Said asymmetric styrene-butadiene-styrene triblock copolymer represented by formula 1 can be prepared by conventional continuous polymerization method in the presence of anion initiator, such as, organic lithium compound.

[0040] The asphalt composition of the present invention comprises i) 100 wt. part of natural asphalt and ii) 0.5–40 wt. part of asymmetric triblock copolymer represented by formula 1, preferably, 1–25 wt. part of asymmetric triblock copolymer represented by formula 1. If the amount of asymmetric triblock copolymer represented by formula 1 is less than 0.5 wt. part, this triblock copolymer cannot make a role as asphalt modifier, because it cannot fully express the function of polymer. On the other hand, if the amount of asymmetric triblock copolymer represented by formula 1 is more than 40 wt. part, this triblock copolymer can result in extremely high viscosity, which causes the decline of dispersion between asphalt and modifier as well as the decline of liquidity by the delay of dispersion. Further, in this case, the mechanical cracking or thermal decomposition of binder can be occur.

[0041] The amount of sulfur in modified asphalt composition can be 0.1–20 wt. part as to 100 wt. part of styrene-butadiene-styrene block copolymer, preferably, 1–10 wt. part.

[0042] As described above, styrene-butadiene-styrene triblock copolymer represented by formula 1 has asymmetric styrene blocks. Of course, it has excellent ductility in low temperature, which results in excellent ductility and thermal stability at low temperature and the resistance to permanent deformation at high temperature.

EXAMPLES

[0043] The present invention can be explained more concretely by following examples. However, the scope of present invention shall not be limited by following examples.

Preparation Example 1
Preparation of Asymmetric Styrene-butadiene-styrene Triblock Copolymer

[0044] 2L of reactor is fully purged with argon gas. Then, 900 g of purified cyclohexane and 20 g of styrene are added with maintaining the temperature at 70°C. Cyclohexane solution (1.3 M concentration) containing 2 mmol of n-butyllithium(BuLi) as initiator is added to reactor, and polymerization reaction is initiated. After 10 minutes lapse at the highest polymerization temperature, 170 g of butadiene is added to initiate polymerization. After 5 minutes lapse at the highest polymerization temperature, 10 g of styrene is added to initiate polymerization. The polymerization is terminated by addition of a small amount of methanol to reaction solution. After completely removing the activity of leaving polymer, addition of anti-oxidant is carried out.

[0045] The removal of solvent in the obtained polymer mixture solution is carried out using steam. Then, cream type of asymmetric styrene-butadiene-styrene triblock copolymer is obtained. Finally, remaining solvent and water is dried by roll mill.

Preparation Example 2
Preparation of Asymmetric Styrene-butadiene-styrene Triblock Copolymer

[0046] 2L of reactor is fully purged with argon gas. Then, 900 g of purified cyclohexane and 25 g of styrene are added with maintaining the temperature at 70°C. Cyclohexane solution (1.3 M concentration) containing 2 mmol of n-butyllithium(BuLi) as initiator is added to reactor, and polymerization reaction is initiated. After 10 minutes lapse at the highest polymerization temperature, 170 g of butadiene is added to initiate polymerization. After 5 minutes lapse at the highest polymerization temperature, 5 g of styrene is added to initiate polymerization. The polymerization is terminated by addition of a small amount of methanol to reaction solution. After completely removing the activity of leaving polymer, addition of anti-oxidant is carried out.

[0047] The removal of solvent in the obtained polymer mixture solution is carried out using steam. Then, cream type of asymmetric styrene-butadiene-styrene triblock copolymer is obtained. Finally, remaining solvent and water is dried by roll mill.

Preparation Example 3
Preparation of Asymmetric Styrene-butadiene-styrene Triblock Copolymer

[0048] 2L of reactor is fully purged with argon gas. Then, 900 g of purified cyclohexane and 28 g of styrene are added with maintaining the temperature at 70°C. Cyclohexane solution (1.3 M concentration) containing 2 mmol of n-butyllithium(BuLi) as initiator is added to reactor, and polymerization reaction is initiated. After 10 minutes lapse at the highest polymerization temperature, 170 g of butadiene is added to initiate polymerization. After 5 minutes lapse at the highest polymerization temperature, 2 g of styrene is added to initiate polymerization. The polymerization is terminated by addition of a small amount of methanol to reaction solution. After completely removing the activity of leaving polymer, addition of anti-oxidant is carried out.

[0049] The removal of solvent in the obtained polymer mixture solution is carried out using steam. Then, cream type of asymmetric styrene-butadiene-styrene triblock copolymer is obtained. Finally, remaining solvent and water is dried by roll mill.

Preparation Example 4
Preparation of Asymmetric Styrene-butadiene-styrene Triblock Copolymer

[0050] 2L of reactor is fully purged with argon gas. Then, 900 g of purified cyclohexane and 29 g of styrene are added with maintaining the temperature at 70°C. Cyclohexane solution (1.3 M concentration) containing 2 mmol of n-butyllithium(BuLi) as initiator is added to reactor, and polymerization reaction is initiated. After 10 minutes lapse at the highest polymerization temperature, 170 g of butadiene is added to initiate polymerization. After 5 minutes lapse at the
highest polymerization temperature, 1 g of styrene is added to initiate polymerization. The polymerization is terminated by addition of a small amount of methanol to reaction solution. After completely removing the activity of leaving polymer, addition of anti-oxidant is carried out.

Preparation Example 5
Preparation of Asymmetric Styrene-butadiene-styrene Triblock Copolymer

[0052] 2L of reactor is fully purged with argon gas. Then, 900 g of purified cyclohexane and 40 g of styrene are added with maintaining the temperature at 70° C. Cyclohexane solution (1.3 M concentration) containing 2 mmol of n-butyllithium(BuLi) as initiator is added to reactor, and polymerization reaction is initiated. After 10 minutes lapse at the highest polymerization temperature, 155 g of butadiene is added to initiate polymerization. After 5 minutes lapse at the highest polymerization temperature, 5 g of styrene is added to initiate polymerization. The polymerization is terminated by addition of a small amount of methanol to reaction solution. After completely removing the activity of leaving polymer, addition of anti-oxidant is carried out.

[0053] The removal of solvent in the obtained polymer mixture solution is carried out using steam. Then, cream type of asymmetric styrene-butadiene-styrene triblock copolymer is obtained. Finally, remaining solvent and water is dried by roll mill.

Comparative Preparation Example 1
Preparation of Linear Styrene-butadiene Block Copolymer

[0054] 2L of reactor is fully purged with argon gas. Then, 900 g of purified cyclohexane and 15 g of styrene are added with maintaining the temperature at 70° C. Cyclohexane solution (1.3 M concentration) containing 2 mmol of n-butyllithium(BuLi) as initiator is added to reactor, and polymerization reaction is initiated. After 10 minutes lapse at the highest polymerization temperature, 170 g of butadiene is added to initiate polymerization. After 5 minutes lapse at the highest polymerization temperature, 15 g of styrene is added to initiate polymerization. The polymerization is terminated by addition of a small amount of methanol to reaction solution. After completely removing the activity of leaving polymer, addition of anti-oxidant is carried out. The removal of solvent in the obtained polymer mixture solution is carried out using steam. Then, white color of linear styrene-butadiene block copolymer is obtained. Finally, remaining solvent and water is dried by roll mill.

[0055] The properties of block copolymers prepared in preparation examples and comparative preparation examples are measured by following protocol. The results are shown in Table 1.

Comparative Preparation Example 2
Preparation of Linear Styrene-butadiene Block Copolymer

[0056] 2L of reactor is fully purged with argon gas. Then, 900 g of purified cyclohexane and 30 g of styrene are added with maintaining the temperature at 70° C. Cyclohexane solution (1.3 M concentration) containing 2 mmol of n-butyllithium(BuLi) as initiator is added to reactor, and polymerization reaction is initiated. After 10 minutes lapse at the highest polymerization temperature, 140 g of butadiene is added to initiate polymerization. After 5 minutes lapse at the highest polymerization temperature, 30 g of styrene is added to initiate polymerization. The polymerization is terminated by addition of a small amount of methanol to reaction solution. After completely removing the activity of leaving polymer, addition of anti-oxidant is carried out. The removal of solvent in the obtained polymer mixture solution is carried out using steam. Then, white color of linear styrene-butadiene block copolymer is obtained. Finally, remaining solvent and water is dried by roll mill.

[0057] The properties of block copolymers prepared in preparation examples and comparative preparation examples are measured by following protocol. The results are shown in Table 1.

Comparative Preparation Example 3
Preparation of Radial Styrene-butadiene Block Copolymer

[0058] 2L of reactor is fully purged with argon gas. Then, 900 g of purified cyclohexane and 60 g of styrene are added with maintaining the temperature at 70° C. Cyclohexane solution (1.3 M concentration) containing 7 mmol of n-butyllithium(BuLi) as initiator is added to reactor, and polymerization reaction is initiated. After 10 minutes lapse at the highest polymerization temperature, 140 g of butadiene is added to initiate polymerization. After 5 minutes lapse at the highest polymerization temperature, 1.8 mmol of SiCl₄ is added to initiate coupling reaction. The polymerization is terminated by addition of a small amount of methanol to reaction solution. After completely removing the activity of leaving polymer, addition of anti-oxidant is carried out. The removal of solvent in the obtained polymer mixture solution is carried out using steam. Then, white color of radial styrene-butadiene block copolymer is obtained. Finally, remaining solvent and water is dried by roll mill.

[0059] The properties of block copolymers prepared in preparation examples and comparative preparation examples are measured by following protocol. The results are shown in Table 1.

Analysis of Molecular Weight

[0060] The analysis of molecular weight is measured by high performance liquid chromatography “separation’s module Waters 2690” as well as by detector “differential refractometer Waters 410”. Following are analysis conditions. The temperature of column is 41° C, solvent is THF and flow rate is 0.3 mL/min. Column is used by linear connection of divinylbenzene Styragel HR 5E, HR 4, HR 2. The standard of polystyrene is employed to measure the difference of refraction rate by the refraction detector.

Analysis of Micro Structure and Amount of Copolymer

[0061] Analysis of Molecular Weight

[0062] The analysis of molecular weight is measured by high performance liquid chromatography “separation’s module Waters 2690” as well as by detector “differential refractometer Waters 410”. Following are analysis conditions. The temperature of column is 41° C, solvent is THF and flow rate is 0.3 mL/min. Column is used by linear connection of divinylbenzene Styragel HR 5E, HR 4, HR 2. The standard of polystyrene is employed to measure the difference of refraction rate by the refraction detector.

[0063] Analysis of Micro Structure and Amount of Copolymer

[0064] Analysis of Molecular Weight
Measurement of Solution Viscosity

The measurement of copolymer solution viscosity is carried out using polymer solution dissolved with toluene in a concentration of 5.23 wt %. At 25° C, constant temperature, the viscosity is measured by Ubbelohde viscosity meter under the condition that constant K is 0.09048 mm²/s².

<table>
<thead>
<tr>
<th>Example Pre.</th>
<th>Styrene Amount</th>
<th>Percentage of Blocks(%)</th>
<th>Molecular Weight(Mn)</th>
<th>Solution Viscosity(cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre. Ex. 1</td>
<td>14.8</td>
<td>92</td>
<td>192,000</td>
<td>21</td>
</tr>
<tr>
<td>Pre. Ex. 2</td>
<td>14.5</td>
<td>83</td>
<td>201,000</td>
<td>21</td>
</tr>
<tr>
<td>Pre. Ex. 3</td>
<td>15.2</td>
<td>88</td>
<td>190,000</td>
<td>20</td>
</tr>
<tr>
<td>Pre. Ex. 4</td>
<td>14.8</td>
<td>78</td>
<td>195,000</td>
<td>21</td>
</tr>
<tr>
<td>Pre. Ex. 5</td>
<td>22.3</td>
<td>95</td>
<td>202,000</td>
<td>18</td>
</tr>
<tr>
<td>Com. Pre.</td>
<td>14.8</td>
<td>91</td>
<td>198,000</td>
<td>21</td>
</tr>
<tr>
<td>Ex. 1</td>
<td>29.8</td>
<td>97</td>
<td>195,000</td>
<td>12</td>
</tr>
<tr>
<td>Ex. 2</td>
<td>30.1</td>
<td>96</td>
<td>299,000</td>
<td>21</td>
</tr>
</tbody>
</table>

Examples 1–5

Measurement of Modified Asphalt Composition

Each 21 g of obtained polymers in Preparation Examples 1–5 are added to 600 g of natural asphalt at 180° C. in a melting phase. After mixing them high performance mixer, polymer modified asphalt binders are prepared. Further, 0.6 g of sulfur is also added and agitated for 20 minutes to prevent the phase separation of rubber due to the difference of density and incompatibility. Finally, styrene-butadiene-styrene modified asphalt compositions are prepared.

For measuring the ductility of asphalt composition, the testing materials are prepared according to the process comprising the steps of i) heating the modified asphalt composition, ii) pouring the melting composition to the mold, and iii) cooling the composition (KS M 2254). To measured ductility, measurement protocol (KS M 2254) comprising the steps of i) inserting the testing materials into 5° C. water bath, ii) forcing tensile strength at both ends in a velocity of 3 cm/min, and iii) measuring the length when the testing materials are divided are employed.

Table 2 shows the softening point and ductility length of testing materials.

<table>
<thead>
<tr>
<th>Example Pre.</th>
<th>Amount of block copolymer modifier (wt. part)</th>
<th>Softening point (° C.)</th>
<th>Before RTFO(Rolling thin film oven) (5° C., cm)</th>
<th>After RTFO(Rolling thin film oven) (5° C., cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex. 1</td>
<td>3.5</td>
<td>74</td>
<td>39.5</td>
<td>24.5</td>
</tr>
<tr>
<td>Ex. 2</td>
<td>3.5</td>
<td>77</td>
<td>36.1</td>
<td>26.1</td>
</tr>
<tr>
<td>Ex. 3</td>
<td>3.5</td>
<td>79</td>
<td>36.4</td>
<td>26.1</td>
</tr>
<tr>
<td>Ex. 4</td>
<td>3.5</td>
<td>92</td>
<td>40.5</td>
<td>26.5</td>
</tr>
<tr>
<td>Ex. 5</td>
<td>3.5</td>
<td>94</td>
<td>33.8</td>
<td>24.8</td>
</tr>
<tr>
<td>Com. Ex. 1</td>
<td>3.5</td>
<td>71</td>
<td>36.5</td>
<td>22.8</td>
</tr>
<tr>
<td>Com. Ex. 2</td>
<td>3.5</td>
<td>93</td>
<td>36.4</td>
<td>16.1</td>
</tr>
<tr>
<td>Com. Ex. 3</td>
<td>3.5</td>
<td>97</td>
<td>32.4</td>
<td>12.5</td>
</tr>
</tbody>
</table>

As shown in Table 2, an asphalt compositions comprising asymmetric styrene-butadiene-styrene block copolymer prepared in Example 4 and 5 show higher softening point compared to Example 1, which means that the resistance against permanent deformation has been maintained at high temperature. The softening points of compositions prepared in Example 4 and 5 are similar to that of Comparative Example 2 having high styrene amount. Further, comparing to Comparative Example 2, the compositions prepared in Example 4 and 5 show that the ductility after rolling thin film oven has been remarkably enhanced. Of course, it means that the ductility of at low temperature is also enhanced, while the crack caused by fatigue or thermal deformation is declined. Therefore, the asphalt composition prepared in Examples can be regarded as suitable asphalt composition for pavement of road. On the other hand, comparing radial type polymer in Comparative Example 3, the asphalt compositions prepared in Examples show the better ductility, while softening points are not better than that of radial type polymer.

What is claimed is:

1. A modified asphalt composition showing excellent ductility and thermal stability at low temperature and the resistance to permanent deformation at high temperature comprising i) 100 wt. part of natural asphalt; and ii) 0.5–40 wt. part of asymmetric triblock copolymer having number average molecular weight of 20,000–1,000,000 represented as following formula 1.

\[ A-B-A' \]  

(formula 1)

wherein

A represents a vinyl aromatic polymer block having number average molecular weight of 8,000–30,000;

B represents a conjugated-diene polymer block or a conjugated-diene copolymer block having a small amount of vinyl aromatic monomers; and
A' represents a vinyl aromatic polymer block having number average molecular weight of 500–5,000;
wherein the weight amount of A and A' block is 5–40 wt % of total A-B-A' triblock copolymer, and the percentage of vinyl aromatic monomer in the block A+A' as to total vinyl aromatic monomer amount in A-B-A' is 50–98%.

2. The modified asphalt composition according to claim 1, wherein said vinyl aromatic polymer block (A or A') comprises monomers at least one selected from the group consisting of styrene, α-methylstyrene, o-methylstyrene, p-methylstyrene and p-tert-butylstyrene.

3. The modified asphalt composition according to claim 1, wherein said vinyl aromatic monomer is a styrene.

4. The modified asphalt composition according to claim 1, wherein said conjugated-diene polymer block (B) is a homopolymer block consisting of butadiene or a tapered block consisting of most of butadienes and a small amount of conjugated diene monomers.

5. The modified asphalt composition according to claim 1, wherein the number average molecular weight of said compound of formula 1 is 50,000–400,000.

6. The modified asphalt composition according to claim 1, wherein said asphalt composition comprises i) 100 wt. part of natural asphalt and ii) 1–20 wt. part of asymmetric triblock copolymer represented by formula 1.

7. The modified asphalt composition according to claim 1, further comprising linear or radial block copolymer.

8. A use of modified asphalt composition of claim 1, for pavement of road or manufacturing water proof sheet.

* * * * *