Improving the Aging Resistance of Styrene-Butadiene-Styrene Tri-Block Copolymer and Application in Polymer-Modified Asphalt

Yintao Li,[1,2] Linfan Li,[1] Yan Zhang,[1,2] Sufang Zhao,[1,2] Leidong Xie,[1] Side Yao[1]

[1]Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China
[2]Graduate School, Chinese Academy of Sciences, Beijing 100049, China

ABSTRACT: Thermal oxidation process of styrene-butadiene-styrene (SBS) copolymer was studied by using a variety of analytical and spectroscopic methods including thermal analysis, dynamic mechanical analysis and FTIR spectroscopy. The experimental results indicate that the thermal oxidation process of SBS is a free radical self-catalyzed reaction containing four steps (initiation, growth, transfer, and termination of the chain) with both crosslinking and scission and the latter is confirmed to be the main process. The antioxidants 1010 as scavenger of free radicals and 168 acting decomposition of hydroperoxides were used to improve the oxidation aging resistance of SBS copolymer. It has been found that synergic effect of 1010 and 168 may be the best in practice and 0.2 wt % 1010 + 0.4 wt % 168 can effectively prevent SBS from the thermal oxidation at certain temperature. Furthermore, the aging resistance of the SBS-modified asphalt was improved by addition of complex antioxidants. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 754–761, 2010

Key words: SBS; block copolymers; thermal oxidation; antioxidants; polymer-modified asphalt

INTRODUCTION

The poly (styrene-*block*-butadiene-*block*-styrene) tri-block copolymer (SBS) application has been extended constantly due to the production process independent of sulfiding and crosslinking and its outstanding physical and mechanical properties.[1–3] Nowadays it is widely used in the preparation of modified asphalts, which are used in high performance specialty pavements to suppress the noise level and to drain out water readily, among other desirable effects.[4,5] However, due to the sensitivity of the double bonds of PB segment to light, heat and oxide, like butadiene rubber (BR), SBS tends to be degraded by exposure to heat and UV light causing discoloration and surface embrittlement, which would impact its performance.[6] In this case, it is necessary to improve the aging resistance of SBS both during manufacturing and laying of SBS-modified asphalt at high temperature (at least 160°C) in pavement application.

The mechanisms of thermal and mechanical degradation of homo- and copolymers of styrene and butadiene have been studied in the past under different conditions.[7–11] As SBS copolymer contains unsaturated C=C in PB segment, the degradation mechanism is similar to polybutadiene rubbers. The generation of free radicals causing undesirable reactions of the double bonds in PB segment makes its degradation, while various antioxidants are available to reduce the degradation, such as the use of hindered phenols to scavenge the free radicals and the use of phosphites to decompose the hydroperoxides.[11–13] In this article, the variation of reactive groups during the process of thermal oxidation was investigated by Fourier transform infrared and differential scanning calorimetry. In particular, the effect of two kinds of antioxidants on improving the aging resistance of SBS was validated by different methods. Based on this, we will be able to improve resistance of SBS-modified asphalts by adding complex antioxidants.

EXPERIMENTAL

Materials

SBS, Grade 791H, was produced by the Yue yang Petrochemical, China. The antioxidants contained in SBS were extracted by acetone.
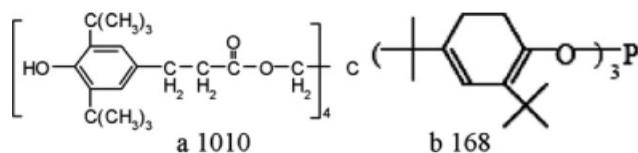
Scheme 1 Molecular structure of the selected antioxidants.

Asphalt, AH-70 paving asphalt, was obtained from Zhenhai Petrochemical, China. The physical properties of asphalt were as follows: penetration, 70 dmm (decimillimetre, 25°C, ASTM D5); softening point, 47.5°C (ASTM D36).

The antioxidants used in this article were Irganox 1010 (pentaerythrityl terakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate]) and Irgafos 168 [tris (2,4-di-*tert*-butylphenyl) phosphite)] from Ciba Company. Their chemical structures are shown in Scheme 1.

Thermal analysis tests analysis

The differential scanning calorimetry (DSC) curves were recorded on a METLER TOLEDO DSC822 apparatus. In the dynamic mode, Nitrogen gas was used to replace the air in the reactor, kept at 80°C for 3 min and then replaced by oxygen with 100 mL/min. The heating rate was 10°C/min from 80 to 250°C. In the static mode, the sample was heated under Nitrogen gas before temperature had been reached at 150°C and switching to an oxygen atmosphere while timing.

Fourier transform infrared analysis

SBS samples were prepared by first dissolving an appropriate amount of polymer in cyclohexane solution to make its concentration to be 10 wt %, and then casting and dying this solution onto a potassium bromide (KBr) thin plate of around 0.1 mm thickness. The samples were aged in ageing experimental oven at 120°C for different time (10, 20, 30, ...120 min) respectively.

The aged samples were characterized by Fourier transform infrared (FTIR) spectroscopy in a transmittance mode on a Vatar 370 FTIR spectrometer (Nicolet, Instrument, Madison, Wisconsin). The FTIR spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and 32 scans.

Rheological measurements

SBS samples were prepared by first dissolving an appropriate amount of polymer in cyclohexane solution to make its concentration to be 10 wt %, and then casting and dying this solution into a polymeric film of 0.2 mm thickness. The resulted film was aged in ageing experimental oven for two hours at 120°C.

Rheological behaviors of the samples were investigated with a strain-controlled rheometer (Advances Rheology Expanded System, TA Instruments, Twin Lakes, Wisconsin). The specimens were processed by a plate vulcanization machine at 160°C to form a layer thickness of about 1 mm. Dynamic temperature tests were performed over the temperature range of 30–160°C with heating rate of 3°C/min under a frequency of 1.0 rad/s and a strain of 1% with parallel plates geometry while the gap was 1 mm. The rheological parameter complex viscosity (η), was collected automatically by RSI Orchestrator software (TA Instruments, Twin Lakes, Wisconsin).

Preparation of modified asphalts

Modified asphalt was prepared using a high shear mixer (made by Weiyu Machine, China) at 170°C and a shearing speed of 3000 rpm. First, 600 g asphalt was heated to make it into fluid in an iron container, and then upon reaching about 170°C, SBS was added into the asphalts with 5 wt % and sheared for 30 min to produce polymer-modified asphalt. 1010 and 168 were added into SBS-modified asphalt with varied amount and sheared for 5 min.

Short-term laboratory aging of SBS-modified asphalt was performed using the Rolling Thin Film Oven Test (RTFOT, ASTM D2872) to simulate the aging process. The standard aging procedures of 163°C for 85 min were used.

RESULTS AND DISCUSSION

Investigation of SBS thermal oxidation invariability in DSC

The oxidation induction time/temperature (OIt/*T*) methods are reported to be a simple method to investigate the stable effectiveness of polymers by several authors.[14–16] Many coworkers have indicated that the oxidation induction time/temperature (OIt/*T*) is a simple method to investigate the stable effectiveness of polymers. The experiments can be conducted in two different modes: dynamic and static. In the dynamic mode, the test sample is heated at a constant heating rate under a pure oxygen gas flow. The OIT is determined by the onset of the oxidation process that is characterized by an exothermic peak in the heat flow-temperature plot. In the static mode, the sample is heated and kept at 150°C under inert gas which is switched to oxygen atmosphere. Then, the OIt can be determined according to the time from switched time to the onset of an exothermic oxidation peak. It has been found that OIt

TABLE I
The DSC OIT Results of SBS with Different Additives

Sample no.	Additives (wt %)	OIT/°C
1	None	149.6
2	0.1%1010	179.4
3	0.2%1010	186.8
4	0.4%1010	189.8
5	0.2%168	155.1
6	0.4%168	159.9
7	0.6%168	161.2

depends on the concentration of antioxidants and their effectiveness.

Thermal stability of the SBS samples was assessed with thermal analysis using DSC and the data is summarized in Table I. Figures 1 and 2 show dynamic DSC oxidation curves of SBS, SBS + 1010, and SBS + 168 from 80 to 250°C with heating rate of 10°C/min, respectively. Pure SBS is noted in the Table I to possess a very low OIT of 149.6°C. The 0.1 wt % additive of the hindered phenol 1010 alone in SBS provides a significant increment with OIT values of 179.4°C. A significant increment with OIT values of 179.4°C was observed with 0.1 wt % additive of the hindered phenol 1010 alone in SBS, and the increment of OIT becomes smooth with the continue increment of hindered phenol 1010 from 0.1 wt % to 0.4 wt % The OIT increases from 155.1°C to 161.2°C with the additive of 168 from 0.2 wt % to 0.6 wt %, which is not significant compared with that of 1010. As mentioned later in this article (Function mechanism of antioxidant), antioxidant hindered phenol 1010 can scavenge free radicals ROO· produced from the oxidation of SBS while the double bond in PB of SBS has been broken to form carbon radicals at a temperature of 150°C, and then the car-

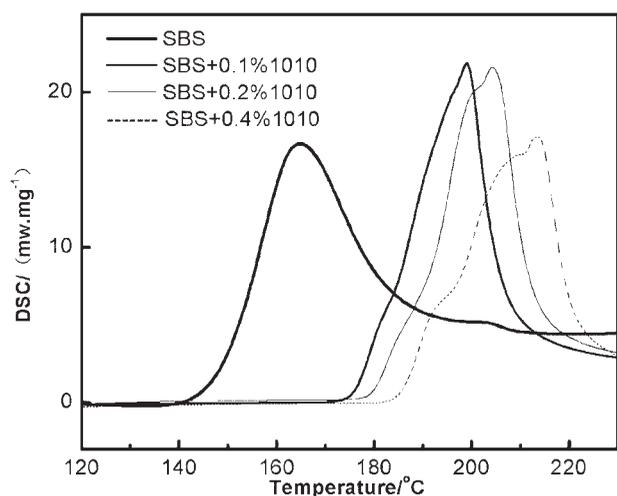**Figure 1** Dynamic DSC oxidation curves of SBS and SBS+ 1010 from 80 to 250°C with heating rate of 10°C/min.
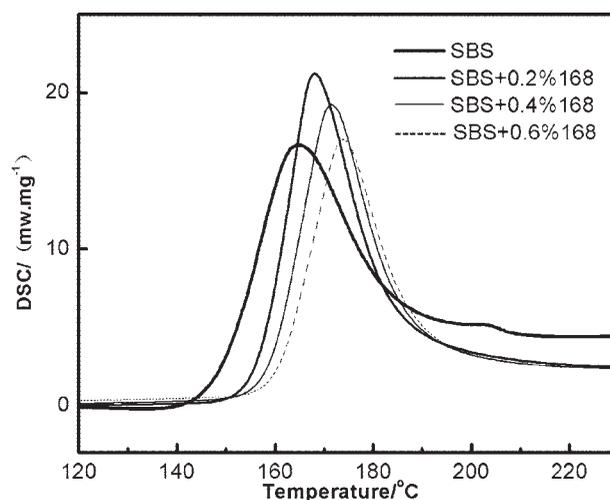
Figure 2 Dynamic DSC oxidation curves of SBS and SBS+ 168 from 80 to 250°C with heating rate of 10°C/min.

bon radicals are transferred into ROO·. Along with the amount of additive 1010 the scavenging effect enhances and the OIT increases. However, at higher temperature, the products of 1010 formed in the scavenging process may be decomposed to form new super oxygen radicals, which will cause further oxidation of SBS. Hence, the antioxidant effects will not be maintained at higher temperature even with more 1010 in SBS. With the 168, one of phosphates, its antioxidant effects is confirmed to be weaker than that of 1010 as it can only scavenge ROOH produced from oxidation of SBS. Anyway, the OIT with the 168 has been determined to be lower than that of 1010 though the added amount is more.

Generally, the complex antioxidants, which mean more than two kinds of antioxidant will be used, have been proposed by technician as there are synergic effects between two antioxidants. In this article, hindered phenol 1010 and phosphate 168 have been added in SBS to confirm the synergic effects. As shown in Figure 3 and Table II there is almost no significant increment of OIT for SBS, which may be due to poor antioxidant performance of 168 at higher temperature. Figure 4 shows the results of OIt measured with the specimens at 150°C in static mode. A little change with the oxidation curve of SBS over 600 S was observed meanwhile the oxidation curve goes smoothly along with amount increment of 168. As listed in Table II, the SBS with addition of 0.2 wt % 1010 specimen have an endothermic peak after 595 S, and the specimen added 0.2% wt 1010 plus 0.2 wt % 168 or 0.2 wt % 1010 plus 0.4 wt %168 has OIt of 635 S or 665 S, respectively, (Table II). It indicates that the synergic effects of 1010 and 168 can somewhat enhance stability of SBS upon the thermal oxidation. But the synergic effect is confirmed to be limited to SBS.
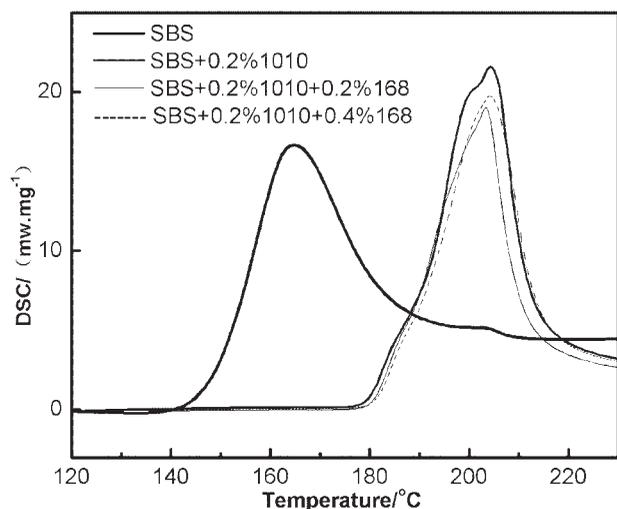
Figure 3 Dynamic DSC oxidation curves of SBS and SBS+ antioxidants from 80 to 250°C with 10°C/min.

Investigation of SBS thermal oxidation invariability in IR

The existence of α-H and C=C in PB segment of SBS results in the higher sensitivity of SBS to light and heat.[12,13] In this article, the change of the groups on molecular chains before and after aging was studied with a FTIR spectrometry.

Figure 5 shows the different FTIR spectra of SBS samples. Compared with the FTIR spectra of SBS before heating, along with the heating at 120°C in oxygen for 30 min a broad absorption band between 3200 and 3600 cm^{-1} as characteristic absorption of hydroxyl group obviously appears. And a new characteristic peaks appear in the range of 1690–1850 cm^{-1} as shown in the inset of Figure 5, which can be assigned to contribution from carbonyl groups, meanwhile the intensity of hydrocarbon vibration and absorption in the range of 2800–3000 cm^{-1} decreases slightly. Furthermore, the details characteristic absorption peak of carbonyl groups summarized in Table III can be proposed to come from Anhydride/lactone/peracids at 1770 cm^{-1}, Aliphatic esters at 1727 cm^{-1} and Unsaturated carbonyls at 1692 cm^{-1}, respectively, identified in the aging process of butadiene rubber.[12,13]

Obviously, the formation of carbonyl group in the thermo-oxidative process of SBS is important event in the change of chemistry structure of SBS in its

TABLE II
The DSC OIT and OIt Results of SBS with Different Additives

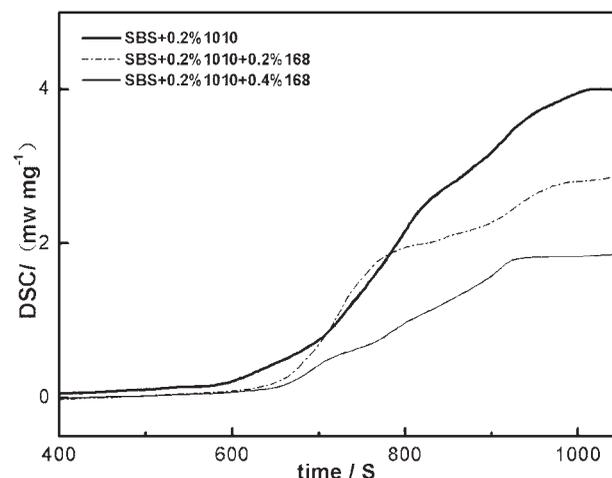| Sample No.	Additives (wt %)	OIT/°C	OIt/S
8	0.2% 1010	186.8	595
9	0.2% 1010 + 0.2% 168	187.2	635
10	0.2% 1010 + 0.4% 168	187.0	665

Figure 4 Static DSC oxidation curves of SBS+ antioxidants at 150°C.

thermal aging. So we try to ascertain the oxidative degree of SBS by the carbonyl groups' conversion using FTIR. As shown in Figure 6 the absorbance of carbonyl groups recorded at different absorption peaks varies along with the aging time. It has been found that the variation is much similar to that of carbonyl groups at 1720 cm^{-1} produced in oxidation of butadiene rubber.[17] The absorbance at 1692 cm^{-1} increases quickly with the heating time and tends to reach its maximum values after 35 min as shown in Figure 6. The absorbance at 1727 cm^{-1} and at 1770 cm^{-1} change with different kinetics, which can be used to confirm that the carbonyl groups formed in thermal oxidation of SBS have three kinds of molecular structure.

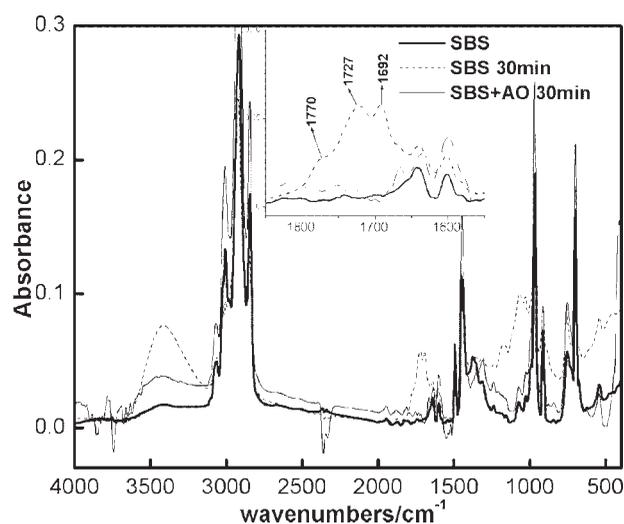For the sample of SBS with additive of complex antioxidants, no obvious new characteristic peaks

Figure 5 FTIR spectra of SBS before heating and SBS+AO and SBS after heating at 120°C for 30 min. The inset: the details of FTIR spectra in the range from 1900 cm^{-1} to 1500 cm^{-1}.

TABLE III
New Major FTIR Absorption Bands in SBS During Oxidation at 120°C

Wave numbers (cm^{-1})	Group	Remark
3440	Hydroxyls	O—H stretch
1770	Anhydride/lactone/peracids	C=O stretch
1727	Aliphatic esters	C=O stretch
1692	Unsaturated carbonyls	C=O stretch

appear in the range of 1690–1800 cm^{-1} was detected during aging although there is a small characteristic peak in the range of 3200–3600 cm^{-1}. It has also been found that the absorbance of carbonyl groups remains smoothly for 120 min heating time as shown in Figure 7. Anyway, it has been revealed that the complex antioxidants (0.2 wt % 1010 + 0.4 wt % 168) can improve the aging resistance of SBS. The related mechanism of antioxidants will be discussed later.

Rheological behavior of Specimens

In this study, dynamic mechanical analysis was employed to characterize the rheological performance of SBS before and after laboratory aging. Rheological parameters [complex viscosity (η)] as a function of temperature for all the samples were determined at 1 rad/s (0.159 Hz) and in a temperature range from 30 to 160°C as shown in Figure 8 with an aged sample heated at 120°C for 120 min.

As we know the double bonds in PB segment of SBS is very sensitive to thermal oxidation. The free radicals formed from breakage of double bonds at high temperature can induce crosslinking or scission. The scission of SBS molecules chain is major process
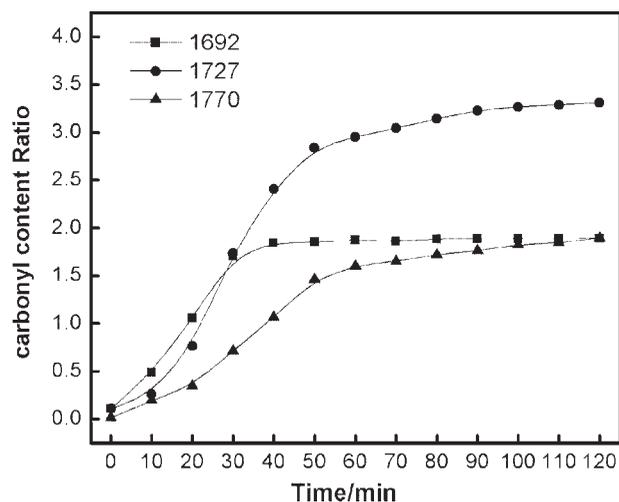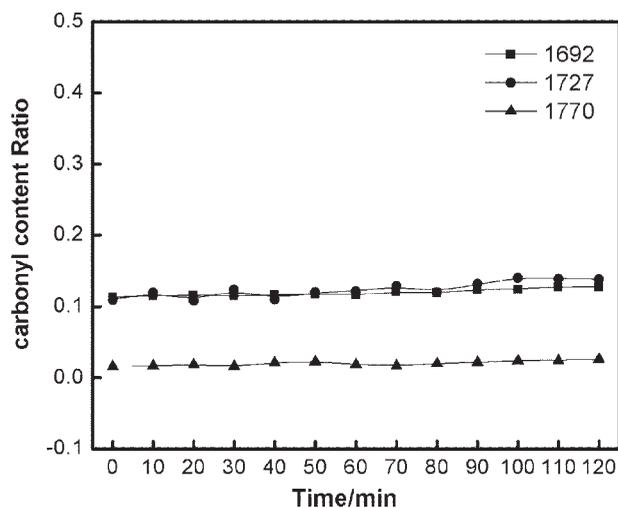

Figure 7 The change of absorbance versus heating time at 120°C recorded at different absorption peak with SBS+ antioxidants.

in its thermal oxidation. And it should occur that the inner friction among the SBS molecules decreases as its molecular weight has been cut down in the scission process. As shown in Figure 8 the complex viscosity (η) in temperature region of 50–160°C decreases rapidly according to the decrement of inner friction compared with that of its nature state. It has been found that the effect of aging is temperature dependent and series of experimental results have not been listed in this article. With the sample SBS + complex antioxidants (0.2 wt % 1010 + 0.4 wt % 168), a little decrement of η has been observed, which indicates that the antioxidants are available to reduce the degradation of SBS during laboratory aging, and it is good agreement with the results obtained by use of DSC and FTIR.

Figure 6 The change of absorbance versus heating time at 120°C recorded at different absorption peak with pure SBS.

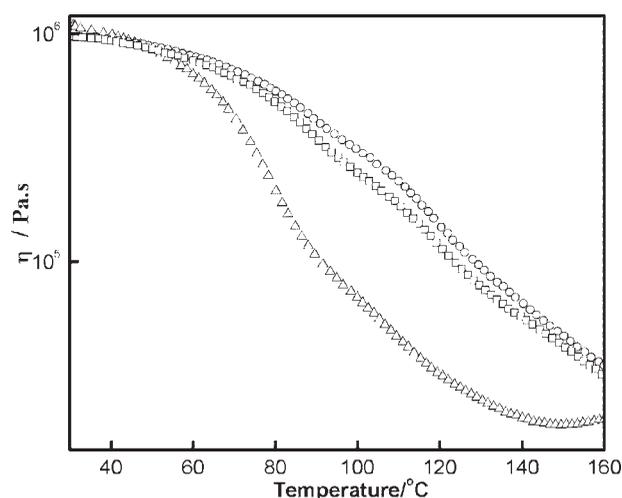**Figure 8** Complex viscosity (η) as a function of temperature at 1 rad/s for SBS before and after aging: ○, SBS; Δ, aged SBS; □, aged SBS+ antioxidants.
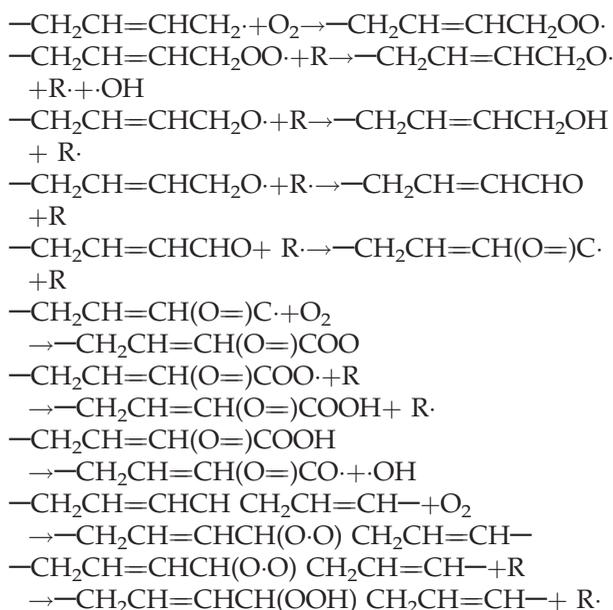
Thermal oxidation mechanism of SBS

The FTIR analysis reveals that both α-H and C=C in PB segment of SBS participate in the thermal oxidation of SBS, producing carbonyl group, ester carbonyl group and anhydride conjugated with double bonds. The mechanism for the thermal oxidation of SBS copolymer can be proposed as following and confirmed by other scientists[11–13]:
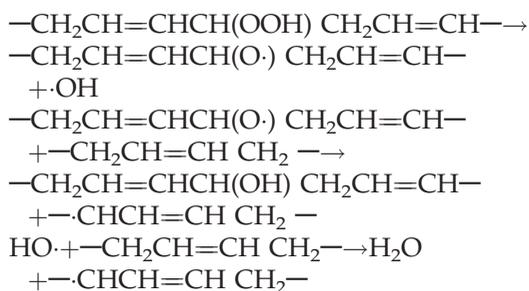
At the first stage, the α-H of PB segment seems to be the initiating point of the oxidation owing to its high activity.

$$—CH_2CH=CHCH_2CH_2CH=CH—$$
$$→—CH_2CH=CHCH·CH_2CH=CH—+·H$$
$$—CH_2CH=CHCH_2CH_2CH=CH—$$
$$→—CH_2CH=CHCH_2·$$
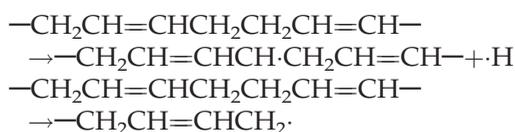
At the second stage, the polymer radicals(R·) are formed initially by exposure to heat or light. Rapid reaction of these radicals with oxygen follows forming peroxy radicals. (R represents $—CH_2CH=CHCH_2—$, R represents $—CH_2CH=CHCH—$)

$$—CH_2CH=CHCH_2·+O_2→—CH_2CH=CHCH_2OO·$$
$$—CH_2CH=CHCH_2OO·+R→—CH_2CH=CHCH_2O·$$
$$+R·+·OH$$
$$—CH_2CH=CHCH_2O·+R→—CH_2CH=CHCH_2OH$$
$$+ R·$$
$$—CH_2CH=CHCH_2O·+R·→—CH_2CH=CHCHO$$
$$+R$$
$$—CH_2CH=CHCHO+ R·→—CH_2CH=CH(O=)C·$$
$$+R$$
$$—CH_2CH=CH(O=)C·+O_2$$
$$→—CH_2CH=CH(O=)COO$$
$$—CH_2CH=CH(O=)COO·+R$$
$$→—CH_2CH=CH(O=)COOH+ R·$$
$$—CH_2CH=CH(O=)COOH$$
$$→—CH_2CH=CH(O=)CO·+·OH$$
$$—CH_2CH=CHCH CH_2CH=CH—+O_2$$
$$→—CH_2CH=CHCH(O·O) CH_2CH=CH—$$
$$—CH_2CH=CHCH(O·O) CH_2CH=CH—+R$$
$$→—CH_2CH=CHCH(OOH) CH_2CH=CH—+ R·$$

At the third stage, the transfer of radical along the polymer chain occurs when $—CH_2CH=CHCH(OOH)CH_2CH=CH—$ approaches to a fixed concentration.

$$—CH_2CH=CHCH(OOH) CH_2CH=CH—→$$
$$—CH_2CH=CHCH(O·) CH_2CH=CH—$$
$$+·OH$$
$$—CH_2CH=CHCH(O·) CH_2CH=CH—$$
$$+—CH_2CH=CH CH_2 —→$$
$$—CH_2CH=CHCH(OH) CH_2CH=CH—$$
$$+—·CHCH=CH CH_2 —$$
$$HO·+—CH_2CH=CH CH_2—→H_2O$$
$$+—·CHCH=CH CH_2—$$

When the concentration of $—CH_2CH=CHCH(OO)CH_2CH=CH—$ and $—CH_2CH=CHCH(O·)CH_2CH=CH—$ remains constant, the dismutation and degradation of SBS occur simultaneously.

$$——CH_2CH=CHCH(O·)CH_2CH=CH—$$
$$→ —CH_2CH=CHCHO + ·CH_2CH=CH—$$

$$—CH_2CH=CHCH(O·O)CH_2— →$$
$$\begin{cases} —CH_2CH=CHCOOH + ·CH_2— \\ —CH_2CH=CHCHOCH_2— + ·OH \end{cases}$$
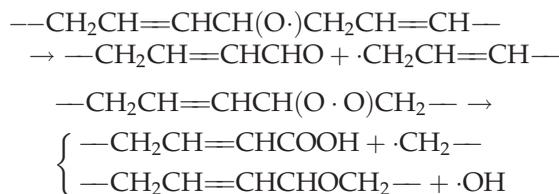
At the fourth stage, the free radical reactions can be terminated via a combination of radical on adjacent polymer molecules, forming carbon–carbon, peroxide or carbonyl crosslink.

$$R·+ R·→R—R$$
$$—CH_2CH=CHCH_2·+—CH_2CH=CH(O=)CO·$$
$$→—CH_2CH=CH(O=)COCH_2CH=CHCH_2—$$
$$—CH_2CH=CH(O=)C·+—CH_2CH=CH(O=)COO·$$
$$→—CH_2CH=CH(O=)COOC(=O)HC=CHCH_2—$$
$$—CH_2CH=CH(O=)C·+—CH_2CH=CH(O=)CO·$$
$$→—CH_2CH=CH(O=)COC(=O)HC=CHCH_2—$$
$$—CH_2CH=CHCH_2O·+—CH_2CH=CHCH_2·$$
$$→—CH_2CH=CHCH_2OCH_2CH=CHCH_2—$$
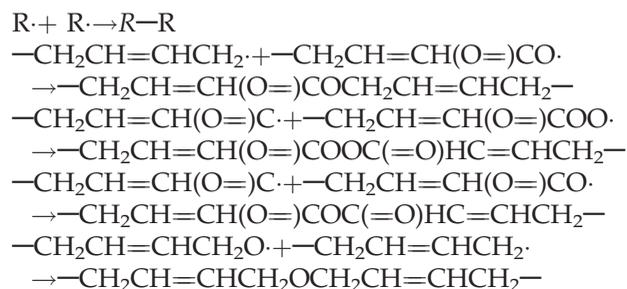
With the double bonds of PB segment of SBS, the oxidation of C=C will induce the formation of ROO· and scission of SBS chains at last.

$$—CH_2CH=CHCH_2—→—CH_2C·HC·HCH_2—$$
$$—CH_2C·H—C·HCH_2—+ O_2→—CH_2C(OO·)$$
$$HC·HCH_2—→—CH_2C(O·) HC(O·)HCH_2$$
$$→2—CH_2C=O$$
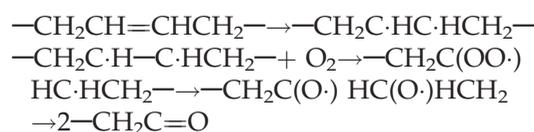
However, the exact microstructures of the degraded SBS involved in thermal oxidation cannot be determined by FTIR alone. And more studies to confirm the oxidation mechanism need to be carried out with new characteristic techniques.

Function mechanism of antioxidant

The characteristics of antioxidants used to stabilize polymers for end-use applications have been reviewed quite extensively in the literature. Gugumus[18] and Zweifel[19] gave excellent reviews of many antioxidants with different function in specific polymers. The kinetics of antioxidant behavior are described by Shlyapnikov et al.,[20] and a review of the chemical activities of polymer stabilizers is given by Pospisil and Nespurek.[21]

The antioxidants, added to polymers to reduce the thermal oxidation, can be divided into main and subordinate antioxidants. In this article, the complex
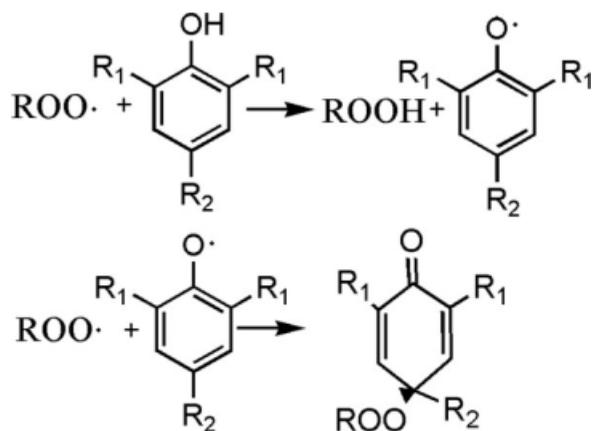
Scheme 2 Function mechanism of antioxidant 1010.

antioxidant has been used to improve the aging resistance of SBS. As a main antioxidant, 1010 is a kind of hindered phenol antioxidant containing —OH functional group [Scheme 1(a)]. The main group participating in the reaction is ArOH which supplies hydrogen atom to terminate active free radical and generates stable free radical ArO· to prevent the chain from radical growth. It means 1010 is a scavenger of free radical. The aryl free radical ArO· generated in this stage is stable and has the ability to capture another ROO· to terminate the second dynamic chain (Scheme 2).

The antioxidation efficiency of the phenol antioxidant has a close correlation with its molecule structure, particularly the number of hydroxyl group. The more *ortho-* and *para-*alkyls of hydroxyl group and branch chains of substituted groups, the higher is the antioxidation efficiency. The introduction of electron repellent groups, like methyl, isopropyl, *tert*-butyl on the vicinal position of hydroxyl group can produce moderate steric effect which avails the alkyl phenol to release hydrogen atoms. Meanwhile, the free radical of phenol oxygen becomes stable because of the super conjugation, giving rise to greatly improve antioxidation efficiency. To the contrary, the introduction of electron withdrawing groups, like aldehyde, carboxyl, nitro, halogen, and etc., can impair the antioxidation efficiency.[22]

In the molecule structure of 1010, R_2 (—$CH_2CH_2COOCH_2C\equiv$) is a strong electron repellent group, which avails the alkyl phenol to release hydrogen atoms, so the antioxidant 1010 has desirable antioxygen efficiency.

Subordinate antioxidants, also known as synergic or preventive antioxidants, can scavenge hydroperoxides formed in thermal oxidation. Generally phosphates have been used as synergic antioxidants for preventing polymer from oxidation. 168, in this article, one kind of phosphates, can be oxidized by ROOH, which will break the radical transfer of the chain in process of thermal oxidation of SBS via following reaction:

$$ROOH + (RO)_3P \rightarrow ROH + (RO)_3P = O$$
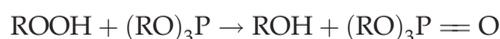
Physical properties of asphalts or polymer-modified asphalts before and after aging

To learn the performance of complex antioxidants, SBS-modified asphalt added with 0.2 wt % 1010 + 0.4 wt % 168 was prepared using AH-70 paving asphalt obtained from Zhenhai Petrochemical. Short-term laboratory aging of SBS-modified asphalt was performed using the Rolling Thin Film Oven Test (RTFOT). The standard aging procedures were carried out at 163°C for 85 min. The properties of aged asphalts are normally characterized by measuring physical/rheological properties (e.g., penetration, softening point and viscosity) before and after artificial aging in the laboratory.

The performance of asphalt has been measured as shown in Table IV with different samples. It has been found that aging has great effect on their physical properties with either base asphalt or polymer-modified asphalt. Additive of complex antioxidants does improve the aging resistance of the polymer-modified asphalt while there is not improvement to asphalt. As we know in the polymer-modified asphalt the SBS can enhance the physical and mechanical properties by forming polymer net in mixing process. Thus, the softening point representing the hardness and ductility representing the mechanical strength of polymer-modified asphalt is higher

TABLE IV
Physical Properties of Unaged and Aged Asphalts in RTFOT

Specimen	Penetration (dmm, 25°C)	Softening point (°C)	Ductility (cm, 5°C)
Base asphalt	68.5	47.0	–
Base asphalt (RTFOT)	36.3	51.5	–
Base asphalt + antioxidants (RTFOT)	35.8	51.4	–
PMA	40.1	83.3	28.0
PMA(RTFOT)	29.8	77.3	11.7
PMA + antioxidants (RTFOT)	32.7	79.2	18.2

than that of asphalt before aging. In the thermal aging process the SBS molecular chains are suffered from the thermal oxidation and the scission of SBS molecular chains occurs. So, the net formed by SBS in polymer-modified asphalt will be broken and induce softening point and ductility decreases in RTFOT after aging. However, with additive of complex antioxidants its physical and mechanical properties have been improved, which confirmed the complex antioxidants of 1010 and 168 can improve aging resistance of SBS-modified asphalt. By the way the parameter of penetration reveals the other physical properties of asphalt and it is also affected by aging and will be discussed in another paper later.

CONCLUSIONS

The thermal oxidation of SBS was studied by DSC, FTIR, and Rheological. It reveals that α-H and C=C in PB segment of SBS are sensitive to thermal oxidation. Four stages including initiation, growth, transfer and termination of free radical are involved in oxidation of SBS. The molecular structure with carbonyl groups is the main oxidized product in aged SBS. OIT and OIt of aged SBS became lower as the scission of SBS chain occurs. The study of SBS rheological behavior confirms that scission of SBS molecules chain is major process during its thermal oxidation process and it makes viscosity of SBS decrease. 1010, one of hindered phenols, can effectively prevent SBS from oxidation via scavenging free radical and 168 as a phosphite can decompose the hydroperoxides. It has been found that the synergic effect of complex antioxidants with 1010 and 168 is limited though the effect of 1010 is better than that of 168. Furthermore, investigation of SBS-modified asphalt in RTFOT has been confirmed that it is available method to improve the aging resistance of polymer-modified asphalt by adding complex anti-

oxidants. And the mechanism involved in thermal oxidation of SBS has been discussed.

References

1. Aggarwal, S. L. Polymer 1976, 17, 938.
2. Wu, C. J Polym Sci Part A: Polym Chem 1993, 31, 3405.
3. Passaglia, E. Polymer 2000, 41, 4389.
4. Becker, M. Y.; Muller, A. J.; Rodriguez, Y. R. J Appl Polym Sci 2003, 90, 1772.
5. McKay, K. W.; Gros, W. A.; Diehl, C. F. J Appl Polym Sci 1995, 56, 947.
6. Bevilacqua, E. M. J Polym Sci Part C 1968, 24, 285.
7. Grassie, N.; Heaney, A. Eur Polym J 1974, 10, 415.
8. Cameron, G. G.; Meyer, L. M.; McWalter, I. T. Macromolecules 1978, 11, 696.
9. Mc Neill, I. C.; Stevenson, W. T. K. Polym Degrad Stab 1985, 10, 247.
10. Schnabel, W.; Levchik, G. F.; Wilkie, C. A.; Jiang, D. D.; Levchik, S. V. Polym Degrad Stab 1999, 63, 365.
11. Allen, N. S.; Edge, M.; Wilkinson, A.; Liauw, C. M.; Mourelatou, D.; Barrio, J.; Martínez-Zaporta, M. A. Polym Degrad Stab 2001, 71, 113.
12. Wang, S. M.; Chang, J. R.; Tsiang, R. C. C. Polym Degrad Stab 1996, 52, 51.
13. Xu, J. B.; Zhang, A. M.; Zhou, T.; Cao, X. J.; Xie, Z. N. Polym Degrad Stab 2007, 92, 1961.
14. Woo, L.; Khare, A.; Blom, H.; Sandford, C.; Ding, S. Y. Thermochim Acta 2001, 367–368, 113.
15. Schmid, M.; Affolter, S. Polym Test 2003, 22, 419.
16. Turi, A.; Ed. Thermal Characterisation of Polymeric Materials, 2nd ed.; Academic Press: San Diego, 1997.
17. Yang, Q. Z. Contemporary Rubber Technology; Sinopec Publications: Peking, 1997.
18. Gugumus, F. In Plastics Additives Handbook, 3rd ed.; Gachter, R.; Muller, H., Eds.; Hanser: New York, 1990.
19. Zweifel, H. Stabilization of Polymeric Materials; Springer-Verlag: New York, 1998.
20. Shylapnikov, Y. A.; Kiryushkin, S. G.; Mar'in, A. P. Antioxidative Stabilization of Polymers; Taylor & Francis: Bristol, PA, 1996.
21. Pospisil, J.; Nespurek, S. In Handbook of Polymer Degradation, 2nd ed.; Hamid, H., Ed.; Marcel Dekker: New York, 2000; Chapter 6.
22. Ma, J. M.; Wu, A. Q. Polym Mater Sci Eng 2004, 20, 46.