Correlation Between Artificial and Natural Weathering Tests on Polystyrene-Block-Polybutadiene-Block-Polystyrene Block Copolymer

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ABSTRACT: The effects of artificial and natural weathering tests on the structure and mechanical properties of polystyrene-block-polybutadiene-block-polystyrene (SBS) block copolymer were studied by spectrophotometry, Fourier Transform Infrared (FTIR) Spectroscopy, hardness measurements, and tensile testing. The correlation between artificial and natural weathering tests was also investigated. The results showed that the surface of SBS became yellow with increasing aging time. FTIR spectra confirmed the formation of carbonyl group in the aging process. The elongation at break, the tensile strength, and the tear strength decreased rapidly in the initial stage of the aging process and then leveled off, while the hardness increased with aging time. The correlation between artificial and natural weathering tests in Wanning and Hailaer, in China, could be expressed in terms of $t_1 = 2.50t_0^{1.99}$ and $t_2 = 1.92t_0^{2.56}$, respectively. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3820–3825, 2008

Key words: correlation; artificial weathering; natural weathering; SBS

INTRODUCTION

Polystyrene-block-polybutadiene-block-polystyrene (SBS) block copolymer is an important type of thermoplastic elastomer. It can be widely used in many fields[1–6] because it has the characteristics of rubber as well as plastic. In recent years, studies mainly concentrated on the physical properties of SBS, such as the deformation behavior,[7,8] the tack behavior,[9] the swelling behavior,[10] and the mechanical properties.[11] However, few studies were found to focus on the correlation between artificial and natural weathering tests on SBS copolymers, especially for the natural weathering in China.

In this work, artificial weathering tests of SBS were carried out with fluorescent UV/condensation weathering apparatus, and natural weathering tests were conducted in Wanning and Hailaer, China. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy was used to study the change in the chemical structures. The effects of aging on the appearance and the mechanical properties were studied by spectrophotometry, hardness measurements, and mechanical testing. A new method is proposed to evaluate the correlation between artificial and natural weathering tests on SBS.

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EXPERIMENTAL

Materials and sample preparation

The material used in this study was polystyrene-block-polybutadiene-block-polystyrene (SBS 4452) provided by Yanshan PetroChem., SINOPEC. This star polymer had a number average molecular weight of 200,000 and a polystyrene content of 40%. The dumbbell shaped specimens were used for this study with dimensions (i.e., typically of length 115 mm, width 25 mm, gauge length 25 mm, and thickness 2.0 mm) as per ISO 37:1994.

Artificial weathering tests

Artificial weathering test was conducted in fluorescent UV/condensation weathering equipment (UV 2000™, USA) according to ASTM G53-1998. The cycle period of the test was 8 h. During this period, the samples were exposed to ultraviolet radiation ($\lambda = 313$ nm) for 4 h at 50°C and then condensation for

TABLE I
Conditions of Natural Weathering Tests

Location	Latitude	Longitude	Exposure angle south	Altitude (m)	Radiation dose (MJ·m^{-2})	Average ambient temperature (°C)	Average relative humidity (%)
Wanning	18°58′ N.L.	110°05′ E.L.	South 45°	12.3	4825.5	24.6	86.0
Hailaer	49°10′ N.L.	120°05′ E.L.	South 45°	647.0	4326.7	−2.5	69.2

4 h at 50°C. The irradiance intensity was 0.55 W m^{-2}.

Natural weathering tests

Natural weathering tests were carried out in Wanning and Hailaer, respectively. Wanning is located in the south of China, on the shore of South China Sea. Hailaer is in the north of China, close to Tropic of Cancer. The climate in Wanning belongs to a typical northern tropical humid zone oceanic climate and that in Hailaer is a frigid and temperate semihumid zone rural climate. The conditions of the natural weathering tests are listed in Table I. Samples were located on test racks made of inert materials and exposed to air up to 540 days. Sampling was performed on days 0, 15, 30, 60, 90, 135, 180, 270, 360, and 540.

Appearance studies

The change of appearance was studied with a spectrophotometer (COLOREYE XTH, USA). The change of color, ΔE, was calculated from the equation $\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$, where ΔL represents the brightness relationship between light and dark, Δa represents the relationship between green and red, and Δb represents the relationship between blue and yellow. The symbol Δ implies the difference between the samples before and after being aged. Yellow index, YI, was calculated from the equation $\text{YI} = \frac{100(1.28X - 1.06Z)}{Y}$, where *YI* represents yellow index, X, Y, and Z represent tristimulus values.

ATR-FTIR analysis

ATR-FTIR spectroscopic analysis was performed on a NICOLET 560 spectrometer (USA). The spectra were taken in the wave-number range from 4000 to 650 cm^{-1} with 32 scans and a resolution of 4 cm^{-1}.

Evaluation of mechanical properties

The mechanical properties were evaluated by hardness, tensile, and tear testing. The indentation hardness (shore A) of the plate samples was determined by means of a pocket hardness meter (type TH200) according to ISO 7619:1986. The tensile specimens were dumb-bell shaped and the tear specimens were angle shaped. The tensile specimens and the tear specimens were tested according to ISO 37:1994 and ISO 34-1:1994 respectively, at room temperature (23°C) and at a cross head speed of 500 mm min^{-1} using a computer-controlled universal testing machine (type WDS). Three samples were examined for each test. A standard deviation of ±3% could be obtained.

RESULTS

Change of appearance

The changes of the appearance of aged SBS samples in both artificial and natural weathering tests (in Wanning and Hailaer) had a similar trend with increasing aging time. The unaged sample was transparent, and the surface was relatively smooth. The surface of the samples turned to yellowish in the initial stage of the weathering tests. With the aging process proceeding, the surface of the sample turned to be more yellow, which was caused by the degradation of the SBS copolymer.[12]

Figure 1 presents the effects of the aging time on ΔE and the yellow index in the artificial weathering test. It can be seen that the longer the aging time, the bigger the values of ΔE and yellow index, which means that the degree of degradation increases with

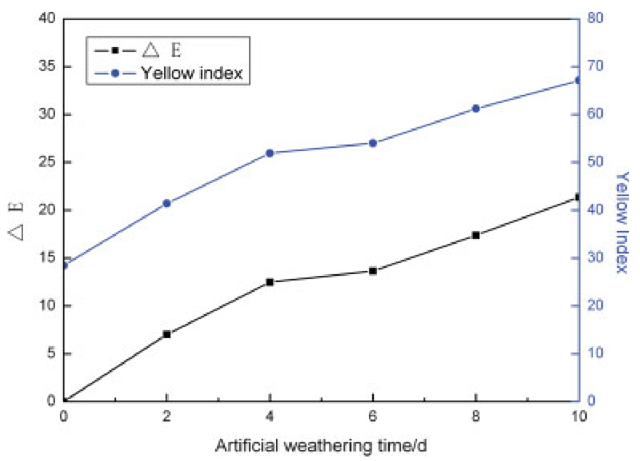

Figure 1 Variation of ΔE and YI against artificial weathering time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

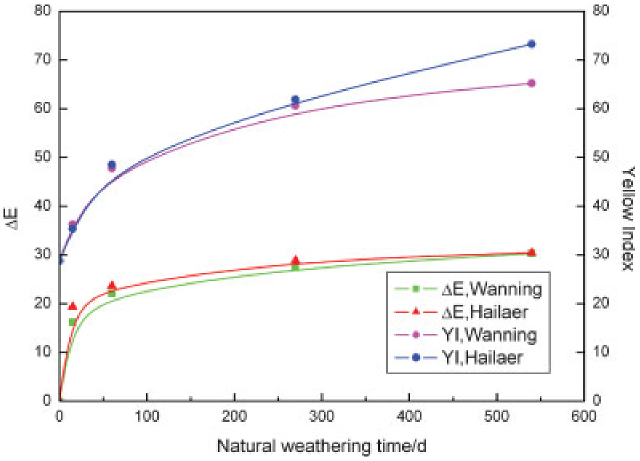

Figure 2 Variation of ΔE and YI against natural weathering time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

aging time. This result is in accordance with that obtained from the change of the sample appearance.

Figure 2 illustrates the variation of ΔE and the yellow index against aging time in natural weathering tests (Wanning and Hailaer). It can be seen that both varied in the same way: increasing sharply initially and then more slowly.

Infrared analysis

The effects of artificial and natural weathering time on SBS surface chemistry were studied by ATR FTIR. Figure 3(a) shows the FTIR spectra of SBS samples before and after artificial weathering for different time periods. The characteristic absorptions of the unaged SBS are illustrated in Table II.

It can be seen that the intensity of the band at 2922 cm^{-1} assigned to the asymmetric stretching vibration of the C—H bond of methylene in the polystyrene segment decreased with increasing aging time. That of the band at 2850 cm^{-1} assigned to the symmetric stretching vibration of the C—H bond also decreased with increase in aging time. Nevertheless, a small peak at 1727 cm^{-1} can be observed in the spectrum of unaged SBS, which could be attributed to the residues of emulsifier and other acidic components from the synthesis of the block copolymer. After artificial weathering for 4 days, a new peak appeared at 1712 cm^{-1}, which is assigned to the stretching vibration of carbonyl group. The intensity of this band increased to a maximum at 6 days of aging and then decreased with increasing aging time, which is probably due to the loss of small molecule product from SBS surface. The bands assigned to E-1, 4-polybutadiene C—H deformation and 1, 2-polybutadiene C—H deformation, which appear at 964 and 910 cm^{-1}, respectively, decreased in intensity with the evolution of the aging process. The intensity of the band at 748 cm^{-1} assigned to polystyrene C—H deformation did not seem to change. So it could be suggested that in the artificial

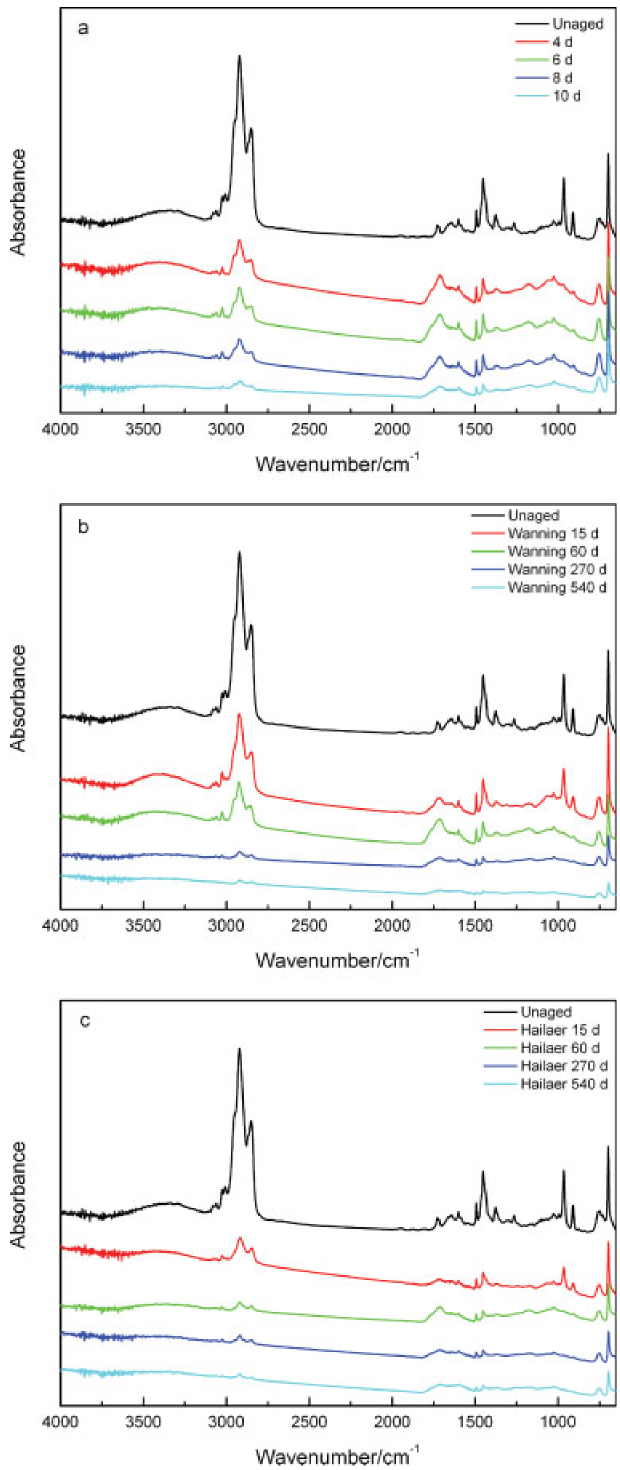

Figure 3 ATR FTIR spectra of SBS samples before and after weathering for different times (a) artificial weathering, (b) natural weathering in Wanning and (c) natural weathering in Hailaer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
FTIR Characteristic Absorption for SBS

Absorption (cm^{-1})	Assignments
2922	CH_2 asymmetric stretching vibration
2850	CH_2 symmetric stretching vibration
1641	1,2-polybutadiene C=C stretching vibration
1601	Polystyrene aromatic C—C stretching vibration
1493 and 1452	Polystyrene CH_2 scissoring vibration
964	E-1,4-polybutadiene C—H deformation vibration
910	1,2-polybutadiene C—H deformation
748 and 698	Polystyrene monosubstituted harmonics C—H deformation vibration

weathering test, the degradation of SBS began from the polybutadiene segment. The formation of ketone resulted in chain scission reactions in the block copolymer.

Figure 3(b,c) present the FTIR spectra of SBS samples before and after natural weathering for different times in Wanning and Hailaer, respectively. It can be seen that the change of FTIR spectra of SBS samples exposed naturally is similar to that of SBS aged in the artificial weathering test. The bands at 2922 and 2850 cm^{-1} decreased more quickly in Wanning that that in Hailaer. After natural weathering for 60 days both in Wanning and Hailaer, the bands at 964 and 910 cm^{-1} disappeared, while the band at 1712 cm^{-1} increased to a maximum. The intensity of the band at 748 cm^{-1} assigned to polystyrene C—H deformation didn't seem to change with increasing exposure time.

Evaluation of mechanical properties

The changes in the mechanical properties of SBS are represented by the following equation:

$$\Delta P\% = \frac{P - P_0}{P_0} \times 100$$

where $\Delta P\%$ represents the percentage change of the mechanical property, P represents the property of aged SBS samples and P_0 represents the property of unaged SBS samples.

Figure 4 presents the effects of artificial weathering on hardness, elongation at break, tensile strength, and tear strength. With increasing aging time, the percentage change of Shore A hardness of SBS samples increased almost linearly. The elongation at break decreased sharply in the initial stage and then leveled off. The tensile strength decreased in the first stage and then kept stable in the range of $6 \sim 7$ MPa. The tear strength behaved in a way similar to those of the elongation at break and the tensile strength. After an aging time of 6 days, the tear strength began to increase very slowly.

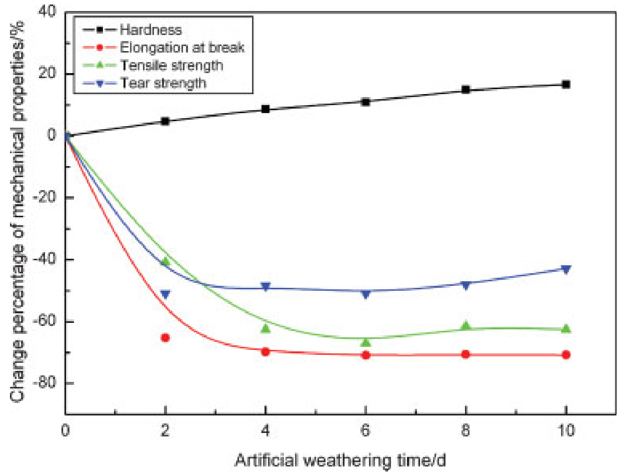

Figure 4 Effect of artificial weathering time on samples mechanical properties. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The effects of natural weathering on the elongation at break and Shore A hardness are illustrated in Figure 5. The elongation at break changed in the same way when the samples were exposed in Wanning and Hailaer. In the initial stages (before 15 days), the elongation at break decreased sharply and then remained stable in the following days. The hardness increased rapidly in the early stages, and then rose continuously in the rest of the aging process. For up to 15 days exposure, the hardness of SBS exposed in Wanning changed in the same as that in Hailaer. After that time, the change of hardness of samples exposed in Wanning was greater than that for samples exposed in Hailaer. Compared with the unaged sample, the hardness of the sample exposed in Hailaer increased 15.19% after 540 days exposure, while the hardness of the sample exposed in Wanning increased 21.52%, which means that in long-term natural weathering

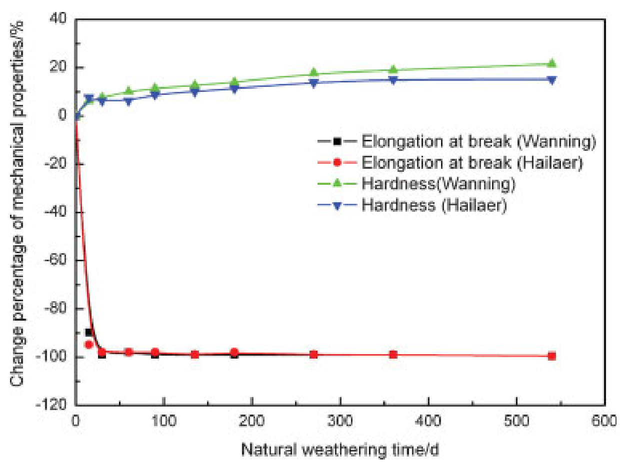

Figure 5 Effect of natural weathering time on samples mechanical properties. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

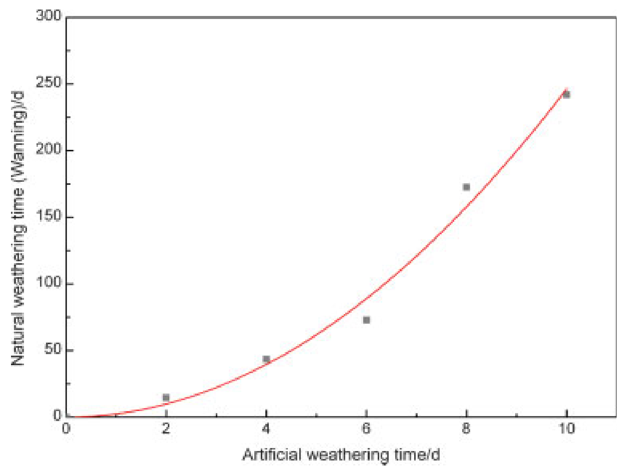

Figure 6 Relationship of t_1 (outdoors, Wanning) and t_0 (indoors). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

test, the samples exposed in Wanning degrade more greatly than those exposed in Hailaer.

The hardening of the samples in the natural weathering tests is related with the climate conditions, such as radiation dose and temperature. In Wanning, the annual average radiation dose is 4825.5 $MJ{\cdot}m^{-2}$, which is 498.8 $MJ{\cdot}m^{-2}$ higher than that in Hailaer. The annual average ambient temperature in Wanning is also higher than that in Hailaer. So the hardening of the samples exposed in Wanning is more serious than that in Hailaer.

DISCUSSION

Change of chemical structures

From the FTIR results it can be seen that both in artificial and natural weathering tests, the bands assigned to polybutadiene segment decreased earlier than that assigned to polystyrene segment. This is because the unsaturated double bond in polybutadiene is sensitive to light and oxygen. The allylic hydrogen is easy to be abstracted under the effect of ultraviolet and oxygen, which causes the formation of free radicals followed by initiating chain reaction. For polystyrene, the conjugated double bonds are relatively more stable hence it is difficult to be broken compared with polybutadiene. So the degradation of SBS arises first from polybutadiene segment.

Correlation between artificial and natural weathering tests by change in hardness of SBS

The acceleration factor is often used to evaluate the correlation between artificial and natural weathering tests.[13] It is calculated through the following equation:

$$F_a = \frac{t_n}{t_a}$$

where F_a is the acceleration factor, t_n is the time when a particular value of the property is achieved in the natural exposure test and t_a is the time when the same value of the property is achieved in the artificial weathering test. However, in our natural weathering tests in Wanning and Hailaer, the change of hardness was not linear, so when different values of hardness are used, different acceleration factors will be obtained.

In our studies, a new method is proposed to evaluate the correlation between artificial and natural weathering tests. The $\Delta P\% \sim t$ curve was fitted by Non-Linear Square Fitting (NLSF), where $\Delta P\%$ is the percentage change of a property and t is the corresponding exposure time in the natural weathering test. The calculated values of $\Delta P\%$ corresponding to different aging times (t_0) in artificial weathering test are inserted into the fitting equation and the corresponding exposure time (t) can be obtained. Then the curve of $t \sim t_0$ can be plotted which can be used to evaluate the correlation between the artificial and natural weathering tests.

In the natural weathering test in Wanning, the relationship between the percentage change of Shore A hardness and the exposure time can be expressed as: $\Delta Ha\% = -12.22 + 5.22 \ln(t_1 + 11.58)$, where the correlation coefficient R is 0.9910, $\Delta Ha\%$ represents the percentage change of Shore A hardness and t_1 represents the exposure time in Wanning. The fitting curve equation of $t_1 \sim t_0$ is $t_1 = 2.50 t_0^{1.99}$, where the correlation coefficient R is 0.9926 (Fig. 6). In the natural weathering test in Hailaer, the relationship between the percentage change of Shore A hardness and the exposure time can be expressed as: $\Delta Ha\% = -7.96 + 3.77 \ln(t_2 + 8.40)$, where the correlation coefficient R is 0.9930 and t_2 represents the exposure time in Hailaer. The fitting curve equation of $t_2 \sim t_0$ is $t_2 = 1.92 t_0^{2.56}$, where the correlation coefficient R is 0.9932 (Fig. 7). From the above analysis it can be seen that the results

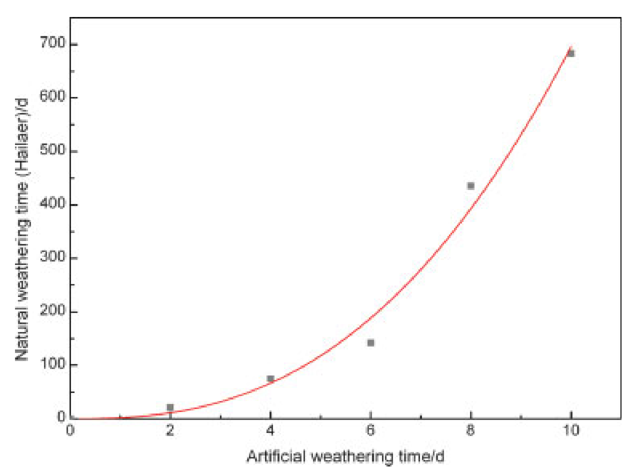

Figure 7 Relationship of t_2 (outdoors, Hailaer) and t_0 (indoors). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

are satisfied to evaluate the correlation between artificial and natural weathering test on SBS samples.

CONCLUSIONS

From artificial and natural weathering tests it can be concluded that SBS is vulnerable to weathering which may have an impact in typical SBS applications such as SBS concrete, HIPS, etc. The strategies to avoid this weathering are to add antioxidants such as chain terminator, peroxide decomposer, and metal deactivator, light stabilizers such as light screening agent, ultraviolet absorber, quencher, and free radical scavenger.

For SBS 4452, artificial weathering test can be used to stimulate natural weathering test for its weathering evaluation, which is helpful to understand the aging behavior and take measures to avoid degradation and elongate its service life in outdoor applications.

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