Article

Research and Improvement of SBS Asphalt-Modifier Content Testing Technology Based on Infrared Spectrum

Ke Zhong 1,2,3, Hao Xu 2, Mingzhi Sun 1,3,*, Guobao Luo 1,3 and Kun Zheng 2

1 Research Institute of Highway Ministry of Transport, Beijing 100088, China
2 School of Civil Engineering, Chongqing Jiaotong University, Chongqing 400074, China
3 Key Laboratory of Transport Industry of Road Structure and Material, Beijing 100088, China
* Correspondence: mz.sun@rioh.cn

Featured Application: A new algorithm for rapid determination of SBS content in asphalt based on infrared spectroscopy was provided and Upgraded method for asphalt sample preparation in FTIR testing in this research.

Abstract: Infrared spectroscopy SBS asphalt-modifier content detection technology has been applied in practical projects, which can effectively ensure the quality of pavement engineering. If the composition ratio of modified asphalt is not clear, the accuracy of the test results will be affected, which is the disadvantage of conventional infrared spectroscopy detection methods. In this paper, the influence of different kinds of additives on the accuracy of the infrared spectrogram and SBS content test was analyzed, and the microscopic mechanism of the effect of additives on the accuracy of SBS modified asphalt content testing was uncovered. Meanwhile, the sample preparation technique was improved and the testing technique was optimized. Results demonstrate that the improved standard curve algorithm eliminates the effect of additives on test accuracy, and the effect of additives on test accuracy was eliminated by improving the standard curve algorithm. Without the addition of additives, the content of the modifier is accurately measured by simplifying the boundary conditions of the test technique. The preparation of samples by the dissolution method has more advantages than the tableting method and can be used as a new sample preparation technology. Improvements in sample preparation techniques and standard curve algorithms improve the safety, convenience, applicability, and accuracy of detection techniques.

Keywords: SBS asphalt-modifier content; infrared spectrum; additive; microscopic mechanism; algorithm improvement

1. Introduction

SBS-modified asphalt is commonly used in asphalt pavement because of its excellent road performance, which can improve the high-temperature resistance, low-temperature resistance, fatigue resistance, and water stability of the asphalt mixture. The performance of SBS asphalt is closely related to the content of SBS in asphalt [1–5]. In practical engineering application, it is found that the SBS-modified asphalt is commonly prepared by adding some waste rubber plastics or some chemical additives to reduce the dosage of SBS, which can affect the road performance of the SBS-modified asphalt, and make the modified asphalt unable to meet the requirements for use [6].

Three index tests can reflect the improvement effect of the modifier on the mechanical properties of asphalt, but the SBS content value cannot be given directly [7]. Meanwhile, the three index tests of all items have a long test cycle, which cannot meet the requirement of a rapid quality evaluation of SBS-modified asphalt. To identify the content of SBS modifier more quickly and accurately, researchers have proposed a variety of SBS content test methods, include an infrared spectrum method, fluorescence microscopy method,
gel permeation chromatography method, thermal weightlessness method, and chemical titration method. Among them, the infrared spectrum method can quantitatively measure the content of SBS modifiers with the characteristics of accuracy, speed, and suitability for on-site testing in the construction project, which is currently the most widely used test method [8–19]. Wei [20] combined the FTIR and HP-GPC tests to estimate the modifier content and obtained a linear regression model of the modifier content. Curtis [21] successfully measured the polymer content in asphalt by infrared spectrum and improved the infrared spectrum to be a method that can be employed for the quantitative analysis of rubber powder content. AASHTO [22] published a test standard for polymer content in asphalt. The Virginia Transportation Commission [23] confirmed that the FTIR test in the AASHTO standard specification can be used to study the polymer content in asphalt.

Although the infrared spectrum is currently the most widely used test method, it still has limitations in some cases. The traditional SBS-modified asphalt uniformly disperses the SBS in the matrix asphalt by physical methods, such as stirring and shearing, which have no obvious chemical changes between SBS and asphalt, just physical mixing. Most types of SBS are thermodynamically incompatible with asphalt, so SBS segregation will occur when stirring is stopped [5]. The storage stability and service performance of SBS-modified asphalt can be improved by adding additives, such as stabilizers and compatibilizers during the mixing process, which make the chemical reactions such as cross-linking and branching between asphalt and SBS to form a network structure [24]. To ensure test accuracy, before the determination of SBS modifier content, it is necessary to fully know the material composition ratio of the sample to be tested and prepare the same asphalt standard sample to calculate the standard curve equation, but in the case of not fully understanding its ratio, it will often affect the accuracy of the test results. If some types of additives are ignored in the preparation of the standard sample, the accuracy of SBS modifier content determination will be influenced. Therefore, to reveal the structural changes and microscopic mechanism of the effect of additives on the accuracy of SBS modifier content determination, find a method to eliminate the effect of additives on the accuracy of the SBS modifier content determination, further improve and upgrade the testing technology from the aspects of the model algorithm and sample preparation method, and improve the convenience and accuracy of technology application will be of great significance to the development of the rapid SBS asphalt-modifier content testing technology.

2. Research Purposes

To determine the influence of additives on the accuracy of SBS modifier content determination, the infrared spectrum method was used in this research to reveal the mechanism of different additives. The improvement method of the testing technology was proposed to simplify its boundary conditions, and the content of SBS modifiers can be accurately measured without adding additives in the preparation of standard samples, which further improves the convenience and applicability of this technology. The research results of this paper can significantly improve the application value of the testing technology of SBS asphalt-modifier content based on the infrared spectrum method.

3. Experimental Scheme Design

3.1. Experimental Materials

Four types of SBS modifiers were used in this experiment, the YH-791 line type, YH-792 line type, 3411 star type, and 1475 star type. Two types of matrix asphalts were used in this experiment, the SW 70# and XP 70#. At present, the commonly used physical additive is compatibilizer, and the reactive additive is stabilizer. Four types of additives were used in this experiment: compatibilizer (number 1) and stabilizer (number 2) from Dongying Mantec Petroleum Chemical Co., Ltd., and compatibilizer (number 3) and stabilizer (number 4) from Dalian Yunhai Rock Asphalt Co., Ltd. The basic physical parameters of the material are shown in Tables 1 and 2.
Table 1. Technical indicators of matrix asphalt and aging bitumen.

| Sample     | Penetration at 25°C/0.1 mm | Soften Point/°C | Ductility at 15°C/cm | Viscosity at 135°C/Pa·s |
|------------|----------------------------|-----------------|----------------------|-------------------------|
| SW70#      | 73                         | 50.0            | >100                 | 0.368                   |
| XP70#      | 73                         | 53.0            | >100                 | 0.378                   |

Table 2. Technical parameters of SBS modifier.

| Technology Index | YH-791 | YH-792 | 3411  | 1475  |
|-----------------|--------|--------|-------|-------|
| Block ratio (S/B) | 30/70  | 40/60  | 30/70 | 40/60 |
| Volatile (%) ≤   | 0.70   | 0.70   | 0.25  | 0.25  |
| Ash (%) ≤        | 0.20   | 0.20   | 0.10  | 0.20  |

3.2. Sample Preparation

The test was conducted in four groups; the first group used SW 70# matrix asphalt and YH-791 linear SBS modifier, the second group used SW 70# matrix asphalt and 1475 star SBS modifier, the third group used XP 70# matrix asphalt and YH-792 linear SBS modifier, and the fourth group used XP 70# matrix asphalt and 3411 star SBS modifier. The standard samples of SBS-modified asphalt for each group were prepared with 2%, 3%, 4%, 5%, and 6% SBS content, and three types of test samples with stabilizer, compatibilizer, and non-additive were prepared with 4% SBS content.

The matrix asphalt and SBS modifier were sheared at 180 ± 10°C for 40 min using an emulsifying shearer with a speed of 5500 r/min, then swelling in an oven at 180°C for 1 h. The compatibilizer was added to SBS before shearing, and the stabilizer was added before swelling. The required SBS-modified asphalt samples for various experiments were established by this method.

3.3. Sample Test

A kind of dissolution method was prepared in this study to prepare a sample for the infrared spectrum test—see Section 5.1 for details. This sample-preparation method was used for all infrared spectroscopy experiments in this study. The wavenumber range of the infrared spectrum test is from 4000 cm⁻¹ to 400 cm⁻¹. The resolution of the spectrometer was not less than 0.5 cm⁻¹, and the scan number was set as 32 times. Five parallel tests were performed for each sample to ensure the accuracy of the test. Figure 1 demonstrates the infrared spectrum of the modified asphalt mixed with 4% SBS modifier. Figure 2 demonstrates the infrared spectra of different types of modified asphalt with 4% SBS content at 966 cm⁻¹.

![Infrared spectra of modified asphalt with different types of SBS modifiers.](image-url)
As can be seen from Figures 1 and 2, the infrared spectra of the four types of SBS-modifier-modified asphalt were different. Taking the modified asphalt with 4% SBS content as an example, the peak area of different modified asphalts at 966 cm$^{-1}$ varies greatly. The concentration of the substance was directly proportional to the peak area; therefore, the content of SBS modifier was analyzed by the peak area at 966 cm$^{-1}$. To eliminate the error of using a single characteristic peak, the characteristic peak area at 1377 cm$^{-1}$ of the base asphalt was calculated, and the SBS content was quantitatively analyzed by the peak area ratio ($A_{966}/(A_{966} + A_{1377})$). The peak area value is the average of five test results.

Methods of measuring peak areas: the peak area consists of troughs and crests. The peak area measurement should include the entire wavenumber range of the absorption peak. Baseline correction was required in the actual calculation to ensure the accuracy. Connecting the lowest points of the troughs on both sides of the absorption peak is the corrected baseline. The blue part in Figure 3a is the peak area before baseline correction, and the blue part in Figure 3b represents the peak area after baseline correction.

3.4. Data Process

First, read the characteristic peak area at 966 cm$^{-1}$ and 1377 cm$^{-1}$ for the obtained infrared spectrum, and then calculate the ratio of the peak areas of the two characteristic peaks, namely $A_{966}/(A_{966} + A_{1377})$. The integration range of the peak area at 966 cm$^{-1}$ is 985 cm$^{-1}$–955 cm$^{-1}$, and the integration range of the peak area at 1377 cm$^{-1}$ is 1400 cm$^{-1}$–1355 cm$^{-1}$. Finally, the standard curve model is established by linear fitting through the least square method as Equation (1):

$$Y = aX + b$$  \hspace{1cm} (1)

where $Y$ is the SBS content of the modified-asphalt samples, $X$ is peak area ratio, $a$ and $b$ are two coefficients. This equation is the standard curve model. The linear correlation of the
standard curve model is evaluated by analyzing the correlation coefficient $R^2$ to determine whether the model meets the SBS content detection requirements. The SBS content (X value) of modified asphalt can be obtained by substituting the $A_{966}/(A_{966} + A_{1377})$ peak area ratio (Y value) of the sample into the standard curve.

4. Results Analysis

4.1. Establishment of the Standard Curve Model

Four groups of SBS-modified asphalt standard samples with different content of 2%, 3%, 4%, 5%, and 6% were detected by the infrared spectrum. The standard curve model was established by linear fitting with the characteristic peak area ratio $A_{966}/(A_{966} + A_{1377})$ and SBS content as shown in Figure 4.

![Figure 4. SBS standard curve model.](image)

The four groups of linear correlation coefficients $R^2$ are 0.9982, 0.977, 0.9942, and 0.9948. The closer $R^2$ is to 1, the better the linear correlation. The $R^2$ of the four groups are all above 0.995, which proves that the curves fit well and meet the test requirements.

4.2. Verification of the Accuracy of the Standard Curve Model

The standard curve in Figure 4 is used to test the 4% SBS-modified asphalt samples without additives, and the test results are shown in Table 3.

| Test Sample | SBS Modifier Content | Additives Amount | $A_{966}/(A_{966} + A_{1377})$ | Test Results |
|-------------|----------------------|-----------------|-------------------------------|--------------|
| First group | 4%                   | 0               | 0.1245                        | 3.95%        |
| Second group| 4%                   | 0               | 0.0765                        | 3.93%        |
| Third group | 4%                   | 0               | 0.1152                        | 3.94%        |
| Fourth group| 4%                   | 0               | 0.0822                        | 4.08%        |

It can be seen from Table 3 that the errors of the four groups are $-0.05\%$, $-0.07\%$, $-0.06\%$, and $+0.08\%$, all within the required error range of $\pm0.1\%$, which meets the test requirements of SBS content detection. It proves that the standard curve models are all correct and can be used for SBS content determination after adding additives.
4.3. Effect of Physical Additives on the Test Accuracy of SBS Content

4.3.1. Experimental Results and Analysis

Four groups of 4% SBS-modified asphalt with compatibilizers ① and ③ are tested by the infrared spectrum. The test results are shown in Table 4 after calculating the peak area ratio and substituting them into the standard curve in Figure 4. Considering the adding of additives, the actual SBS content needs quality correction.

**Table 4. Test results of SBS-modified asphalt with compatibilizer.**

| Compatibilizer Number | Test Sample | A966/(A966 + A1377) | Compatibilizer Content | Test Results | Actual SBS Content | Error |
|-----------------------|-------------|---------------------|------------------------|--------------|-------------------|-------|
| ①                     | First group | 0.1207              | 2.7%                   | 3.84%        | 3.89%             | −0.05%|
|                       | Second group| 0.0747              | 2.7%                   | 3.84%        | 3.89%             | −0.05%|
|                       | Third group | 0.1139              | 2.7%                   | 3.89%        | 3.89%             | 0.00% |
|                       | Fourth group| 0.0793              | 2.7%                   | 3.93%        | 3.89%             | +0.04%|
| ③                     | First group | 0.1198              | 3%                     | 3.78%        | 3.88%             | −0.10%|
|                       | Second group| 0.0770              | 3%                     | 3.98%        | 3.88%             | +0.10%|
|                       | Third group | 0.1161              | 3%                     | 3.97%        | 3.88%             | +0.09%|
|                       | Fourth group| 0.0786              | 3%                     | 3.89%        | 3.88%             | +0.01%|

After considering the influence caused by the quality of the compatibilizer, the actual SBS modifier content is shown in Table 4: the content of No. ① compatibilizer was 2.7%, resulting in an actual SBS modifier content of 3.89%, and the actual errors of the four groups respectively were −0.05%, −0.05%, 0.00%, and +0.04%, and all of them are within ±0.1%. The content of No. ③ compatibilizer was 3.0%, resulting in the actual SBS modifier content of 3.88%, and the actual errors of the four groups respectively were −0.10%, +0.10%, +0.09%, and +0.01%, and all of them are within ±0.1%. It proves that the addition of compatibilizer has no effect on the content determination accuracy of the SBS modifier when using the peak area ratio A966/(A966 + A1377).

4.3.2. Mechanism Analysis

The infrared spectrum of the first group of SBS-modified asphalt at 966 cm$^{-1}$, whether it contains added compatibilizers, is shown in Figure 5, and the peak-area test results are shown in Table 5.

![Figure 5. Infrared spectra of SBS-modified asphalt with and without compatibilizer at 966 cm$^{-1}$](image-url)
As can be seen from Figure 5, the characteristic peak area at 966 cm\(^{-1}\) of the modified asphalt with the compatibilizer added is smaller because the addition of the compatibilizer increases the total mass of the SBS-modified asphalt, which is equivalent to diluting the SBS-modified asphalt. The actual content of the agent will be relatively reduced, resulting in a slight decrease in the peak area ratio. The data in Table 5 prove that the addition of compatibilizer did not cause the change of the characteristic peak area at 966 cm\(^{-1}\), while 966 cm\(^{-1}\) is the characteristic peak of butadiene, which represents the out-of-plane vibration of trans =CH bond in butadiene. The area of the characteristic peak at 966 cm\(^{-1}\) did not change, indicating that the trans =C–H bond in butadiene in SBS did not change quantitatively, and there was no change in the chemical bond.

The components of compatibilizer used commonly are aromatic, saturated, or two mixtures of them, which belong to the four components of asphalt [25]. During the production and storage process of SBS-modified asphalt, the volatilization of saturated and aromatic components will be caused, so using compatibilizer to supplement these two components can slow down the separation of SBS-modified asphalt and matrix asphalt. In Figure 6, the aromatic component in the compatibilizer mainly acts on the polystyrene segment of SBS, and, according to the principle of similar polarity, swelling occurs in the polystyrene microregion. By swelling, the distance between the polystyrene molecular chains will be increased, the molecular force between the segments is reduced, and its motion capacity is enhanced. Because of the intensified movement of polystyrene microdomains, the continuous phase of polybutadiene is more dispersed, the area of SBS increases, and the dispersion of SBS in the asphalt is more uniform, which increases the compatibility of SBS in asphalt. It can be seen from the mechanism of the compatibilizer that the adding of compatibilizer does not cause changes in the chemical bond and molecular structure of the SBS, so the compatibilizer belongs to the physical additive. From the above, it can be concluded that after removing the error caused by the quality of the compatibilizer, the adding of compatibilizer will not cause the change of characteristic peak area and affect the test accuracy.

![Figure 6. Structure of SBS modifier.](image)

**Table 5. Test result of peak area ratio.**

| Test Sample  | 4% SBS Content | Sample with Compatibilizer ① | Sample with Compatibilizer ③ | Peak Area Ratio within the Allowable Error Range |
|--------------|----------------|-------------------------------|-------------------------------|-----------------------------------------------|
| First group  | 0.1232         | 0.1207                        | 0.1198                        | 0.1193–0.1259                                 |
| Second group | 0.0786         | 0.0747                        | 0.0770                        | 0.0739–0.0777                                 |
| Third group  | 0.1193         | 0.1139                        | 0.1161                        | 0.1115–0.1166                                 |
| Fourth group | 0.0831         | 0.0793                        | 0.0786                        | 0.0769–0.0805                                 |

4.4. Effect of Reactive Additive on the Test Accuracy of SBS Content

4.4.1. Experimental Results and Analysis

Four groups of 4% SBS-modified asphalt with stabilizers ② and ④ are tested by the infrared spectrum. The test results are showed in Table 6 after calculating the peak area
After considering the influence caused by the quality of the stabilizer, the actual SBS modifier content is shown in Table 6: the content of the No. ② stabilizer was 0.2%, resulting in the actual SBS modifier content of 3.99%, and the actual errors of the four groups respectively were −0.56%, −0.53%, −0.47%, and −0.49%, and all exceeded ±0.1%. The content of No. ④ stabilizer was 0.25%, resulting in the actual SBS modifier content of 3.99%, and the actual errors of the four groups were −0.89%, −0.74%, −1.24%, and −1.79%, and all exceeded ±0.1%. It proves that the adding of stabilizer has a significant effect on the test accuracy of the SBS modifier content when using the peak area ratio of A966/(A966 + A1377).

4.4.2. Mechanism Analysis

The infrared spectrum of the first group of SBS-modified asphalt at 966 cm\(^{-1}\) whether it contains added stabilizer are shown in Figure 7, and the peak area test results are shown in Table 7.

![Infrared spectrum of SBS-modified asphalt with and without stabilizer at 966 cm\(^{-1}\).](image)

**Figure 7.** Infrared spectrum of SBS-modified asphalt with and without stabilizer at 966 cm\(^{-1}\).
As can be seen from Figure 7, the characteristic peak area at 966 cm\(^{-1}\) is significantly reduced after adding the stabilizer. The data in Table 7 prove that the added stabilizer produces a large experimental error and far exceeds ±0.1%. It proves that the adding of the stabilizer caused a change in the characteristic peak area at 966 cm\(^{-1}\); that is to say, the number of trans =CH bonds in polybutadiene represented by 966 cm\(^{-1}\) in the SBS modifier has changed greatly, so it can be concluded that the C-H bond here has broken and other chemical bonds have been formed, which cause the obvious change of characteristic peak area at 966 cm\(^{-1}\).

The commonly used stabilizers in the market are mainly elemental sulfur, polysulfide, or sulfur-containing cross-linking agent. The structure of butylene is shown in Figure 8. There are three chemical bonds in the existing polybutadiene that may react with the stabilizer, which are the C=C double bond in position 1 at butadiene, the =C-H bond represented by the characteristic peak at 966 cm\(^{-1}\) in position 2, and the C-H bond in the methylene group of position 3. Under the action of the stabilizer, SBS will produce self-crosslinking. Because the C=C double bond of the polybutadiene segment is active, the double bond will break, and the breaking double bonds produce self-crosslinking, resulting in the spatial network structure. In addition to the self-crosslinking, the C=C double bond in butadiene will break into a single bond and branch with other functional groups in asphalt to achieve the stability of the chemical bond. The C-H bond in methylene and the =C-H bond represented by the 966 cm\(^{-1}\) characteristic peak in the infrared spectrum will also break and lose the H atom under the action of additives, and the H atom combines with the heteroatom functional group in asphalt to form a new chemical bond, namely an SBS–asphalt graft. Because the chemical reaction between SBS and asphalt results in the reduction in the =C-H bond represented by 966 cm\(^{-1}\) in the infrared spectrum, so the characteristic peak area at 966 cm\(^{-1}\) of the SBS will decrease with the adding of stabilizers, while the characteristic peak area at 1377 cm\(^{-1}\) in the base asphalt will not change, so the peak area ratio A966/(A966 + A1377) in the SBS content test will be reduced; therefore, it will cause an error in the test results. Therefore, it can be concluded from the above that the adding of stabilizer will affect the test accuracy of SBS modifier content.

| Test Sample | 4% SBS Content | Sample with Stabilizer 1 | Sample with Stabilizer 2 | Peak Area Ratio within the Allowable Error Range |
|-------------|----------------|--------------------------|--------------------------|-----------------------------------------------|
| First group | 0.1232         | 0.1075                   | 0.0964                   | 0.1224−0.1290                                  |
| Second group| 0.0786         | 0.0675                   | 0.0634                   | 0.0757−0.0795                                  |
| Third group | 0.1193         | 0.1046                   | 0.0850                   | 0.1139−0.1190                                  |
| Fourth group| 0.0831         | 0.0717                   | 0.0450                   | 0.0786−0.0822                                  |

Figure 8. Structure of butadiene.
5. The Improvement of Sample-Preparation Method and Algorithms

5.1. The Improvement of Sample-Preparation Method

The method before improvement is the tablet-pressing method: to grind the irregular potassium bromide crystal block into powder in advance, press the potassium bromide powder into a wafer by using the tableting machine, and then heat the asphalt to be tested, which is coated on the potassium bromide wafer to complete the preparation of the test sample.

The method after improvement is the dissolution method: in the experiment, 1 g~2 g asphalt is taken from an SBS–asphalt sample and put into a glass container; trichloroethylene of approximately eight times the weight of asphalt is taken into the container to fully dissolve the asphalt. The asphalt standard samples need to be completely dissolved, and there is no insoluble matter in the solution. Then, the glass dropper is used to drop the dissolved SBS-modified asphalt onto the potassium bromide wafer. After trichloroethylene volatilizes, a thin and uniform transparent SBS-modified asphalt film will be formed on the potassium bromide wafer, as shown in Figure 9.

![Test sample prepared by the dissolution method.](image)

Through comparative research, the dissolution method has the following advantages over the tablet-pressing method:

1. It is necessary to heat the asphalt to the melting state in the tablet-pressing method. The repeated heating of asphalt will cause asphalt aging and then affect the test results. The dissolution method does not require heating and avoids such errors.

2. Under manual operation, it is very difficult to coat the thick, uniform, transparent asphalt film on the potassium bromide wafer. The dissolution method makes use of the volatility of trichloroethylene and the tension of the solution itself, so the asphalt film obtained will be thinner and more uniform, which is more convenient for manual operation.

The experimental results by using the dissolution method are shown in Figure 9 and Table 8. The SBS modifier is YH-791. The SBS content of test sample is 4%.

### Table 8. Quantitative test results of SBS modifier.

| Modifier Model | Number of Scans | A966/(A966 + A1377) | Test Results | Average Value |
|----------------|-----------------|---------------------|--------------|---------------|
| YH-791         | 1               | 0.1233              | 3.92%        |               |
|                | 2               | 0.1238              | 3.93%        |               |
|                | 3               | 0.1230              | 3.91%        |               |
|                | 4               | 0.1252              | 3.97%        | 3.95%         |
|                | 5               | 0.1277              | 4.01%        |               |

According to Figure 10, the linear correlation coefficient $R^2$ is 0.9982, which has a good linear correlation. According to Table 6, it can be seen that the test error is 0.05%, which
meets the allowable error range of ±0.1%. The accuracy is high enough, so it can be used as the basis for the quantitative determination of SBS content. From the above, it can be concluded that the dissolution method has more excellent accuracy, safety, convenience, and applicability, which can be used as an upgrade and improvement of the sample-preparation method in the infrared spectrum SBS content test technology.

![Figure 10. Standard curve of YH-791.](image)

5.2. The Improvement of Model Algorithm

Reactive additives will reduce the number of =C–H bonds in polybutadiene, and the peak area ratio in the infrared spectrum will be significantly reduced. This paper analyzes the infrared spectra of SBS asphalt with different types of additives and proposes a new 699 cm\(^{-1}\) characteristic peak representing SBS. The infrared spectrum of the first group of SBS-modified asphalt, whether it contains additives at 699 cm\(^{-1}\), is shown in Figure 11.

![Figure 11. Infrared spectra of SBS modified asphalt, whether it contains additives at 699 cm\(^{-1}\).](image)

As can be seen from Figure 11, the characteristic peak area of different types of SBS-modified asphalt basically does not change at 699 cm\(^{-1}\). By analyzing the infrared spectrum and the structure of the SBS modifier, the characteristic peak at 699 cm\(^{-1}\) was determined as a new characteristic peak to detect the SBS content. The 699 cm\(^{-1}\) is the characteristic peak of styrene, which belongs to the out-of-plane vibration of the C–H bond in the benzene ring in styrene. The benzene ring is not a C=C unsaturated double-bond structure, but an overall large \(\pi\)-bond structure, which leads to a relative stability overall, and chemical reactions occur with difficulty. Therefore, when 699 cm\(^{-1}\) is used as the characteristic peak of SBS-modified asphalt, the test is not easily covered by the additives.
Four groups of SBS-modified asphalt standard samples with different content of 2%, 3%, 4%, 5%, and 6% were detected by the infrared spectrum. The standard curve is established by linear fitting with the characteristic peak area ratio A699/(A699 + A1377) and SBS content as shown in Figure 12.

![Figure 12](image)

**Figure 12.** Standard curve of SBS content test.

The linear correlation coefficients $R^2$ of the four groups are 0.9951, 0.9998, 0.9979, and 0.9989. The $R^2$ are all above 0.99, which proves that the curves fit well and meet the test requirements.

The standard curve in Figure 12 is used to test the 4% SBS-modified asphalt samples without additives, and the test results are shown in Table 9.

**Table 9.** Test results of 4% SBS-modified asphalt without additives.

| Test Sample  | SBSModifier Content | Additive Amount | $A699/(A699 + A1377)$ | Test Results |
|--------------|---------------------|-----------------|-----------------------|--------------|
| First group  | 4%                  | 0               | 0.082569              | 3.94%        |
| Second group | 4%                  | 0               | 0.042574              | 3.99%        |
| Third group  | 4%                  | 0               | 0.083124              | 4.09%        |
| Fourth group | 4%                  | 0               | 0.043060              | 4.04%        |

It can be seen from Table 9 that the errors of four groups are $-0.06\%, -0.01\%, +0.09\%$, and $+0.04\%$, all within the required error range of $\pm 0.1\%$. It proves that the standard curve model is accurate and can be used for the SBS content test.

Four groups of 4% SBS-modified asphalt with additives (1), (2), (3), and (4) were tested by the infrared spectrum. Table 8 shows the detection results after calculating the peak area ratio $A699/(A699 + A1377)$ and substituting them into the standard curve in Figure 11.

After considering the influence caused by the quality of the additives, the actual SBS modifier content is shown in Table 10: the content of No. (1) compatibilizer was 2.7%, resulting in the actual SBS modifier content of 3.89%, and the actual errors of the four groups were $-0.07\%$, $-0.01\%$, $+0.05\%$, and $+0.10\%$, and all of them are within $\pm 0.1\%$. The content of No. (2) stabilizer was 0.2%, resulting in the actual SBS modifier content of 3.99%, and the actual errors of the four groups were $-0.04\%$, $+0.01\%$, $+0.08\%$, and $+0.10\%$, all of them are within $\pm 0.1\%$. The content of No. (3) compatibilizer was 3.0%, resulting in the actual SBS modifier content of 3.88%, and the actual errors of the four groups respectively were $-0.03\%$, $-0.07\%$, $+0.10\%$, and $-0.07\%$, all of them are within $\pm 0.1\%$. The content of No. (4) stabilizer was 0.25%, resulting in the actual SBS modifier content of 3.99%,
and the actual errors of the four groups were $-0.08\%$, $-0.10\%$, $+0.10\%$, and $-0.07\%$, all of them are within $\pm 0.1\%$. It proves that the addition of additives has no effect on the content determination of the SBS modifier when using the peak area ratio of A699/(A699 + A1377). This improved model algorithm can simplify the boundary conditions of sample preparation. It is no longer necessary to consider the influence of additives, and no need to add additives when preparing standard samples, which greatly improves the application convenience of the test technology.

Table 10. Test results of SBS-modified asphalt with additives.

| Additive Number | Test Sample | SBS Modifier Content | A699/(A699 + A1377) | Additive Content | Test Results | Actual SBS Content | Error |
|-----------------|-------------|----------------------|---------------------|-----------------|--------------|--------------------|-------|
| ①               | First group | 4%                   | 0.078445            | 2.7%            | 3.82%        | 3.89%              | $-0.07\%$ |
|                 | Second group| 4%                   | 0.040649            | 2.7%            | 3.88%        | 3.89%              | $-0.01\%$ |
|                 | Third group | 4%                   | 0.079000            | 2.7%            | 3.94%        | 3.89%              | $+0.05\%$ |
|                 | Fourth group| 4%                   | 0.042350            | 2.7%            | 3.99%        | 3.89%              | $+0.10\%$ |
| ②               | First group | 4%                   | 0.082884            | 0.2%            | 3.95%        | 3.99%              | $-0.04\%$ |
|                 | Second group| 4%                   | 0.042930            | 0.2%            | 4%           | 3.99%              | $+0.01\%$ |
|                 | Third group | 4%                   | 0.082771            | 0.2%            | 4.07%        | 3.99%              | $+0.08\%$ |
|                 | Fourth group| 4%                   | 0.044032            | 0.2%            | 4.09%        | 3.99%              | $+0.10\%$ |
| ③               | First group | 4%                   | 0.076733            | 3%              | 3.79%        | 3.88%              | $-0.03\%$ |
|                 | Second group| 4%                   | 0.039168            | 3%              | 3.81%        | 3.88%              | $-0.07\%$ |
|                 | Third group | 4%                   | 0.080241            | 3%              | 3.98%        | 3.88%              | $+0.10\%$ |
|                 | Fourth group| 4%                   | 0.038898            | 3%              | 3.81%        | 3.88%              | $-0.07\%$ |
| ④               | First group | 4%                   | 0.081738            | 0.25%           | 3.91%        | 3.99%              | $-0.08\%$ |
|                 | Second group| 4%                   | 0.040732            | 0.25%           | 3.89%        | 3.99%              | $-0.10\%$ |
|                 | Third group | 4%                   | 0.083214            | 0.25%           | 4.09%        | 3.99%              | $+0.10\%$ |
|                 | Fourth group| 4%                   | 0.040900            | 0.25%           | 3.92%        | 3.99%              | $-0.07\%$ |

6. Conclusions

Based on the current infrared spectrum testing technology of SBS asphalt-modifier content, this paper studies the influence of physical and reactive additives on the test accuracy of SBS modifier content, reveals the micro mechanism of the influence of additives on the test of SBS modifier content, and improves the existing sample preparation technology and model algorithm. The main conclusions are as follows:

(1) The influence of different types of additives on the test accuracy of SBS modifier content was analyzed mainly in this study. The addition of a physical additive has no effect on the test accuracy of the SBS modifier content, but the reactive additive will cause a chemical reaction inside the SBS-modified asphalt, which shows that the addition of reactive additives has a greater influence on the test accuracy of SBS modifier content.

(2) The traditional FTIR test-sample preparation method was improved in this study, and the dissolution method was proposed. Compared with the tablet-pressing method, the dissolution method has improved in safety, convenience, applicability, and accuracy, which can be used as an upgrade and improvement of sample preparation technology in infrared spectrum testing.

(3) Compared with other studies in this field, this research proposes a new algorithm. Based on the 699 cm$^{-1}$ characteristic peak, it can simplify the boundary conditions of sample preparation. There is no need to add additives when preparing standard samples, which greatly improves the application convenience of the test technology.
Author Contributions: Conceptualization, methodology, K.Z. (Ke Zhong) and K.Z. (Kun Zheng); formal analysis, H.X.; investigation, G.L.; resources, K.Z. (Ke Zhong) and K.Z. (Kun Zheng); writing—original draft preparation, M.S. and H.X.; writing—review and editing, K.Z. (Ke Zhong), H.X., M.S., G.L., K.Z. (Kun Zheng); supervision, M.S. All authors have read and agreed to the published version of the manuscript.

Funding: The research work described herein was funded by the Fundamental Research Funds for the Central Research Institute (Grant No. 2020-9030 and No. 2022-9019). This financial support is gratefully acknowledged.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sun, D.Q.; Zhang, L.W. A quantitative determination of polymer content in SBS modified asphalt. Part I: State of the art. Pet. Sci. Technol. 2013, 31, 2636–2642. [CrossRef]
2. Kim, T.W.; Baek, J.; Lee, H.J.; Choi, J.Y. Fatigue performance evaluation of SBS modified mastic asphalt mixtures. Constr. Build. Mater. 2013, 48, 908–916. [CrossRef]
3. Sengul, C.E.; Oruc, S.; Iskender, E.; Aksoy, A. Evaluation of SBS modified stone mastic asphalt pavement performance. Constr. Build. Mater. 2013, 41, 773–783. [CrossRef]
4. Nivitha, M.R.; Prasad, E.; Krishnan, J.M. Ageing in modified asphalt using FTIR spectrum. Int. J. Pavement Eng. 2016, 17, 565–577. [CrossRef]
5. Xiong, P.; Hao, P. Measures and mechanism analysis of improving the storage stability of styrene-butadiene-styrene polymer modified asphalt. J. Tongji Univ. 2006, 34, 613–618.
6. Luo, S.; Tian, J.; Liu, Z.; Lu, Q.; Zhong, K.; Yang, X. Rapid determination of styrene-butadiene-styrene (SBS) content in modified asphalt based on Fourier transform infrared (FTIR) spectrometer and linear regression analysis. Measurement 2019, 151, 107204. [CrossRef]
7. Xiao, F.; Yao, S.; Wang, J.; Wei, J.; Amirkhanian, S. Physical and chemical properties of plasma treated crumb rubbers and high temperature characteristics of their rubberised asphalt binders. Road Mater. Pavement Des. 2020, 21, 587–606. [CrossRef]
8. McCann, M.; Rovani, J.F.; Thomas, K.P. Detection of Polymers in Asphalt Binders. In Transportation and Development Institute Congress 2011: Integrated Transportation and Development for a Better Tomorrow; American Society of Civil Engineers: Chicago, IL, USA, 2011; pp. 514–527.
9. Zofka, A. Evaluating Applications of Field Spectroscopy Devices to Fingerprint Commonly Used Construction Materials; Transportation Research Board: Thousand Oaks, CA, USA, 2013.
10. Xu, T.; Huang, X. Study on combustion mechanism of asphalt binder by using TG–FTIR technique. Fuel 2010, 89, 2185–2190. [CrossRef]
11. Ghavibazoo, A.; Abdelrahman, M.; Ragab, M. Mechanism of Crumb Rubber Modifier Dissolution into Asphalt Matrix and Its Effect on Final Physical Properties of Crumb Rubber–Modified Binder. Transp. Res. Rec. 2013, 2370, 92–101. [CrossRef]
12. Zhang, F.; Yu, J.; Han, J. Effects of thermal oxidative ageing on dynamic viscosity, TG/DTG, DTA and FTIR of SBS-and SBS/sulfur-modified asphalts. Constr. Build. Mater. 2011, 25, 129–137. [CrossRef]
13. Adedeji, A.; Grünfelder, T.; Bates, F.S.; Macosko, C.W.; Stroup-Gardiner, M.; Newcomb, D.E. Asphalt modified by SBS triblock copolymer: Structures and properties. Polym. Eng. Sci. 1996, 36, 1707–1723. [CrossRef]
14. Yang, J.; Muhammad, Y.; Yang, C.; Liu, Y.; Su, Z.; Wei, Y.; Li, J. Preparation of TiO2/PS-rGO incorporated SBS modified asphalt with enhanced resistance against ultraviolet aging. Constr. Build. Mater. 2021, 276, 121461. [CrossRef]
15. Sun, D.Q.; Zhang, L.W.; Zhang, X.L. Quantification of SBS Content in SBS Polymer Modified Asphalt by FTIR; Advanced Materials Research; Bu, J., Wang, P., Ai, L., Sang, X., Li, Y., Eds.; Trans Tech Publications: Zurich, Switzerland, 2011; pp. 953–960.
16. Weigel, S.; Stephan, D. The prediction of asphalt properties based on FTIR and multivariate analysis methods. Fuel 2017, 208, 655–661. [CrossRef]
17. Hasan, M.A.; Mannan, U.; Tarefder, R.A. Determination of Polymer Content in SBS Modified Asphalt Binder Using FTIR Analysis. In Proceedings of the Ninth International Conference on Construction in the 21st Century (CITC 9), Dubai, United Arab Emirates, 5–7 March 2017.
18. Ye, Z.C.; Chen, D.; Ling, C.; Guan, F.Y. Quantifying SBS Content in Modified Asphalt Using Fourier Transform Infrared Spectroscopy; Advanced Materials Research; Huang, Y., Bao, T., Huang, Z., Wang, H., Eds.; Trans Tech Publications: Zurich, Switzerland, 2015; pp. 691–695.
19. Yan, C.; Huang, W.; Xiao, F.; Wang, L.; Li, Y. Proposing a new infrared index quantifying the aging extent of SBS-modified asphalt. Road Mater. Pavement Des. 2018, 19, 1406–1421. [CrossRef]
20. Wei, J.B.; Shull, J.C.; Lee, Y.-J.; Hawley, M.C. Characterization of asphalt binders based on chemical and physical properties. Int. J. Polym. Anal. Charact. 1996, 3, 33–58. [CrossRef]
21. Curtis, C.W.; Hanson, D.I.; Chen, S.T.; Shieh, G.-J.; Ling, M. Quantitative determination of polymers in asphalt cements and hot-mix asphalt mixes. *Transp. Res. Rec.* **1995**, *1488*, 52–61.

22. *AASHTO T 302-2015: Standard Method of Test for Polymer Content of Polymer-Modified Emulsified Asphalt Residue and Asphalt Binders*. AASHTO: Washington, DC, USA, 2015.

23. Defenderfer, S.D. *Detection of Polymer Modifiers in Asphalt Binder; FHWA/VTRC18; Virginia Transportation Research Council*: Charlottesville, VA, USA, 2006.

24. Yuan, J.A.; Zhou, J.P.; Li, Y.Z. Analysis of interaction between SBS and asphalt. *Zhongguo Gonglu Xuebao (China J. Highw. Transp.)* **2005**, *18*, 21–26.

25. Ji, Y.-H.; Guo, S.-H.; Li, R. Compatibility and Stability Mechanism of SBS Modified Asphalt. *Acta Pet. Sin.* **2002**, *18*, 23–29.