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Improved Properties of Weathered Coal and SBR/Weathered Coal Compound Modified Asphalt

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ABSTRACT

Weathered coal (WTC) modified asphalts with improved storage stability are prepared by incorporating styrene-butadiene rubber (SBR). The effects of WTC and SBR/WTC are studied on the storage and physical properties, and morphologies of the modified asphalts. It is found that the WTC has marked effect on the increasing of softening point at the content of 3 wt% while SBR has significant effect on the low temperature (5ºC) properties and improvement of aging resistance at SBR content of 4 wt% in the WTC and SBR/WTC modified asphalts. The morphology of SEM and TEM photographs show that WTC was dispersed relatively uniform in asphalt which indicates compatibility and storage stability are improved by producing a homogeneous phase in modified asphalts. The FTIR analysis show new weak peak areas in modified asphalts indicating physical alteration is the main changes in modified asphalts.

Key Words:

weathered coal;
SBR copolymer;
modified asphalt;
SBR/weathered coal compond;
FTIR.

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INTRODUCTION

Asphalts are widely employed in several applications, but the most important one is related to the paving industry. However, high-temperature rutting and low temperature cracking of asphalt cements or coating layers due to severe temperature susceptibility limit their further application [1,3]. By consideration of increased traffic loads and in order to improve pavement performance, polymer-modified asphalts (PMA) have been developed during the last few decades [4,5]. There are a large variety of polymers currently being used as PMA, such as styrene- butadiene rubber (SBR), styrene-butadiene-styrene triblock copolymer (SBS) and polyethylene (PE) [6-8].

SBR has been widely used as a binder modifier. Elastomers such as SBR has a significant effect on the results of the ductility test at both 4 and 25ºC; while SBR modified asphalts have high ductility at all temperatures, SBS modified asphalts tend to have lower ductility [9]. According to Becker et al., SBR latex polymers increase the ductility of asphalt pavement [10], which allows the pavement to be more flexible and crack resistant at low temperatures, as found by the Florida Department of Transportation. An Engineering Brief from 1987 available at the US Federal Aviation Administration website [11] describes the benefits of SBR modified asphalt in improving the properties of bituminous concrete pavements and seal coats. In this regard, low-temperature ductility, viscosity, elastic recovery adhesive, and cohesive properties of the pavement are improved. SBR modification also increases elasticity, improves adhesion and cohesion, and reduces the rate of oxidation which helps to compensate for hardening and aging problems [12-17].

When a coal bed is exposed to (or located near) the earth surface, it is easily affected by variation of physical and chemical conditions, giving weathered coal (WTC). One typical characteristics of the weathered coal is their extremely high content of so-called regenerated humic acids which are alkali soluble. Formation of weathered coal is affected by rock nature, thickness, carbonization degree of coal, and landscape. Humic acids have a high content of carboxyl group and a low content of phenolic hydroxyl group [18]. Moreover, it has a high fulvic acid content. Study on the weathered coal and humic acids by focusing on their application in modified asphalt which provide low cost compares with other modified asphalts and their influences on the viscoelastic and antioxidative properties of modifiers asphalts is a matter of research.

For a long time, WTC was considered as troublesome waste for its low caloric properties. We may envisage the possibility of disposing WTC within road asphalt. There is large number of WTC storage in many regions of China. WTC storage in Shanxi and Neimenggu Provinces are 80 hundred million and 50 hundred million tons, respectively. Few researchers have reported asphalt/coal mixtures. According to Philippe et al., coal tar modified bitumen tended to disperse the solid particles and promoted their agglomeration [19]. However, there have been no reports about the preparation of the SBR modified asphalt with physicochemical properties and storage stability by using SBR/WTC compound till now. From an economical and environmental standpoint, the use of SBR/WTC modified asphalts is one of the most preferential recycling methods; resulting in greater cost saving, lower energy consumption, and lower environmental pollution.

In the present work, properties of WTC and SBR/WTC modified asphalts were studied by morphology (transmission electron microscopy and scanning electron microscopy) and FTIR analysis of asphalt modified with WTC and SBR/WTC. For comparison, asphalts modified by direct addition of WTC before and after the addition of SBR were also studied. The test design in the study is shown in Figure 1.

EXPERIMENTAL

Materials

Asphalt, AH-90 paving asphalt was obtained from the Lanzhou Petroleum Asphalt Factory (Gansu Province,

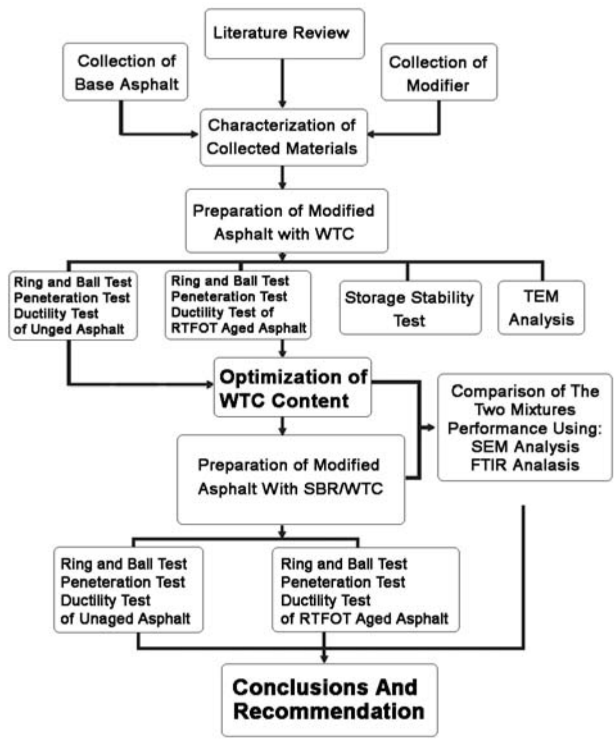

Figure 1. Flow chart of laboratory testing for WTC and SBR/WTC modified asphalts.

China). The physical properties of the asphalt were as follows:

-Penetration: 90 dmm (deci-millimetre, 25ºC, ASTM D 5)

-Softening point: 46.5ºC (ASTM D 36)

-Viscosity: 0.35 Pas (135ºC, ASTM D 4402).

SBR was produced by the Lanzhou Petrochemical Co., Ltd., China. It was a star-like SBR, containing 27.3 wt% styrene, 0.64 wt% water soluble, 0.37 wt% volatile fraction and viscosity (ML_{1+4} 100ºC) 48-55. WTC was purchased from Powder-Material Factory, Xinjiang Province, China.

Preparation of Modified Asphalts

All the modified asphalt samples were prepared using a high shear mixer at 165-175ºC with a shearing speed of 4000 rpm for 50 min. A quantity of 500 g asphalt was heated to be melted in an iron container. After reaching about 175ºC, the modifier (WTC and/or SBR/WTC) was added to the asphalt samples.

Measurement of Physical Properties, Storage Stability Test and FTIR Analysis

The softening points (Ring and Ball test) of different straight and modified asphalt samples were measured according to ASTM D 36. In this test, two disks of asphalts were cast into shouldered rings, and then the disks were trimmed to remove the excess asphalt. After that, the disks were heated at a constant rate (58ºC /min) in a water bath using a special apparatus.

The penetration tests were carried out at 25ºC according to ASTM D 5. The asphalt sample was thermostated in a water bath and the penetration of a standard needle under a standard load (50 g) was measured during 5 s and reported in tenth of millimetre.

Ductility determined at 5ºC by an extensional speed of 1 cm/min in accordance with Chinese specification GB/T 4508.

The storage stability of modified asphalts was measured as follows: some of the prepared modified asphalt was transferred into a glass toothpaste tube (32 mm in diameter and 160 mm in height). The tube was sealed and stored vertically in an oven at 163ºC for 48 h, then taken out, cooled to room temperature, and cut horizontally into three equal sections. The samples taken from the top and bottom sections were used to evaluate the storage stability of the WTC modified asphalts by measuring their softening points. If the difference between the softening points of the top and the bottom sections was less than 2.5ºC, the samples were considered to have good storage stability. If the softening points differed by more than 2.5ºC, the modified asphalt was taken as unstable.

The infrared spectra were recorded with a Nicolet Nexus 670 FT-IR and Nicolet Avatar 360 FTIR spectrometers. The samples were prepared by casting a film onto a sodium chloride (NaCl) window from a 5 w/v % solution in chloroform [20-22].

Standard Ageing Procedure

The ageing of the modified polymer asphalts was performed using two methods. The rolling thin film oven test (RTFOT, ASTM D 2872) simulates the changes in the properties of asphalt during the plant hot mixing and the lay down process. The second method, pressure ageing vessel (PAV) uses the residue from RTFOT test and is representative of the long term ageing due to in situ field ageing [23].

Morphological Analysis

The morphological observations were also performed by both TEM and SEM techniques. PA was immersed in absolute alcohol in a beaker and dispersed by a low power ultrasonic instrument for half an hour. Then a drop of PA/alcohol mixture was taken out from the beaker for morphological observation. The observation was performed on a scanning electronic microscope (SEM, S-450, Japan) with a resolving power of 4.5 μm.

TEM observations were obtained on a JEM-100SX 200 kV field emission TEM with an acceleration voltage of 200 kV. The asphalts samples for TEM study were prepared by evaporating asphalts-ethanol suspensions on a holy carbon coated copper grid. Composites samples for TEM imaging are in the form of 80-100 nm thick thin-sections supported on a copper grid.

Statistical Analysis

Statistical analyses for evaluating the influence of variables on softening point, penetration, and ducti lity (5ºC) at a 0.05 significance level (95% confidence level) were performed using a statistical analysis system (SAS) software package. The variables considered were base asphalt type, type of additive, and ageing of asphalt.

RESULTS AND DISCUSSION

Properties of Asphalt Modified with WTC

Influence of WTC Contents on the Softening Point, Penetration and 5ºC Ductility of Unaged and RTFOT Aged Samples

During the preparation of the asphalts modified with SBR/WTC, the WTC contents would lead to different distributions of SBR and WTC in the asphalt samples which result in changes in the properties of modified asphalts. Therefore, the effect of WTC contents was studied on the properties of modified asphalts.

Table 1 shows the effect of WTC contents on the softening point, penetration, and 5ºC ductility of unaged and RTFOT aged samples. To observe the improvements of different properties in unaged and RTFOT aged modified asphalt samples, their results are given in Table 1. As it is noticed in Table 1, with increasing WTC content, the softening point of the WTC modified asphalts increased which implies that the properties of asphalt have been improved by WTC addition. When the content of WTC was fixed at 3 wt%, the WTC modified asphalt sample showed the highest softening point of 58.0ºC. The softening point of the modified asphalt is significantly promoted when the PS content is not higher than 3 wt%, whereas it slightly decreases when WTC content is 5 wt%.

The penetrations and the low-temperature (5ºC) ductility of the WTC modified asphalt samples decreased slightly (Table 1). By the increasing of WTC contents, the penetration and the ductility of modified asphalt samples have not shown any evident changes. Moreover, there would be no changes in penetration ratio and ductility when RTFOT ageing occurrs.

The results suggest that WTC has a significant effect on the properties of WTC modified asphalt samples by increasing their softening point. While increasing WTC content had little effect on the low temperature (5ºC) properties of modified asphalts. Furthermore, WTC content of 3-4 wt% was probably the upper limit below which fairly high softening point could be achieved.

Effect of SBR Contents on the Softening Point, Penetration, and 5ºC Ductility Properties of Unaged and RTFOT Aged SBR/WTC Modified Asphalt Samples

As the results are shown in Table 1, 3 wt% of WTC is probably an appropriate content of it in WTC modified asphalt. We fixed WTC content at 2 and 3 wt% and used different SBR contents to observe the influence of SBR contents on the properties of SBR/WTC modified asphalts.

Table 2 shows the influence of SBR content on the softening points of SBR/WTC modified asphalts. No significant changes were seen in the softening points by increasing SBR content comparing with the case of the absence of SBR (Table 1). The softening points of SBR/WTC modified asphalts are seemingly independent of the SBR contents. The influence of SBR on the ductility performance of the modified asphalts

Table 1. Influence of WTC contents on the softening point, penetration, and 5ºC ductility of unaged and RTFOT aged samples.

PA and OP content (WT%)	Softening point (ºC)	Penetration (25ºC, dmm)	Ductility (cm, 5ºC)	RTFOT		
				Ductility (cm, 5ºC)	Penetration ratio (25ºC, %)	Weight loss (%)
Control*	47.0	77	6.0	3.0	68	0.40
WTC 1%	54.0	50	4.0	2.2	80	0.05
WTC 2%	54.3	50	2.2	1.5	74	0.12
WTC 3%	58.0	43	3.3	1.7	79	0.10
WTC 5%	57.3	40	3.0	2.0	80	0.05

(*) Base asphalt

Table 2. Influence of WTC contents on the softening point, penetration, and 5ºC ductility of unaged and RTFOT aged of SBR/WTC modified asphalt.

SBR content (wt%)	Softening point (ºC)	Penetration (25ºC, dmm)	Ductility (cm, 5ºC)	RTFOT		
				Ductility (cm, 5ºC)	Penetration ratio (25ºC, %)	Weight loss (%)
Control*	47.0	77.0	6.0	3	68	0.04
SBR2%/WTC2%	55.6	57.2	74	13	78	0.08
SBR3%/WTC2%	56.5	55.4	90	38	80	0.14
SBR4%/WTC2%	56.6	65.2	150	75	76	0.13
SBR2%/ WTC 3%	55.6	57.2	61	15	80	0.09
SBR3%/ WTC 3%	57.3	55.6	78	40	80	0.15
SBR4%/ WTC 3%	57.4	62.8	150	85	85	0.08

(*) Base asphalt

before and after aging with using the RTFO procedure is presented in Table 2. In a research work, Lamontagne et al. have compared the aging with the rolling thin film oven test (RTFOT) and demonstrated that 1 h testing of RTFOT corresponds to two years of road use and further confirmed that the RTFOT test has a moderated effect on the asphalt aging [2].

The influence of SBR on the ductility of the SBR/WTC modified asphalts was dependent on the SBR content. With increasing the SBR content, the 5ºC ductility of the asphalt is dramatically promoted. When the SBR content is higher than 3 wt%, a maximum ductility is reached. The tendency of changes in the ductility after RTFOT ageing closely resembled the changes of unaged samples. With the increase of SBR content, the ductility increases significantly after the application of RTFOT test but not to the same extent as observed in the unaged samples.

Meanwhile, the penetration ratio was increased after the RTFOT process. This indicated that in the SBR(4 wt%) / WTC(3 wt%) modified asphalt, the ductile properties are greatly improved which it modifies the ageing resistance.

It could be concluded that WTC has marked effect on the increasing of softening point while increasing SBR content has marked effect on the low temperature (5ºC) properties and improvement of aging resistance. Therefore, SBR/WTC modified asphalts have the improving effects on increasing softening point and promoting ductility and aging resistance properties.

Storage Properties of WTC Modified Asphalt

The extension of compatibility between the polymer and the asphalt was necessary during storage, pumping, and applying the asphalt and for achieving the expected properties in the pavement [24]. Stability tests can determine whether the interactions created between the polymers and the asphalts during mixing are strong enough to resist a separation of the polymer in the conditions in which it is stored. As mentioned above, WTC had little effect on softening point whereas it had significant effect on low temperature (5ºC) ductility. In this case, storage test was not necessary for SBR/WTC modified asphalt samples. The storage stabilities of WTC modified asphalts were presented in Figure 2. Obvious differences in the softening points were detected in base asphalt, indicating that base asphalt was unstable. While, in the presence of WTC contents, the storage stability of WTC modified asphalt was improved significantly. No marked differences in the softening points were observed in the modified asphalt samples.

Morphology

The study of morphology by TEM and SEM tech-

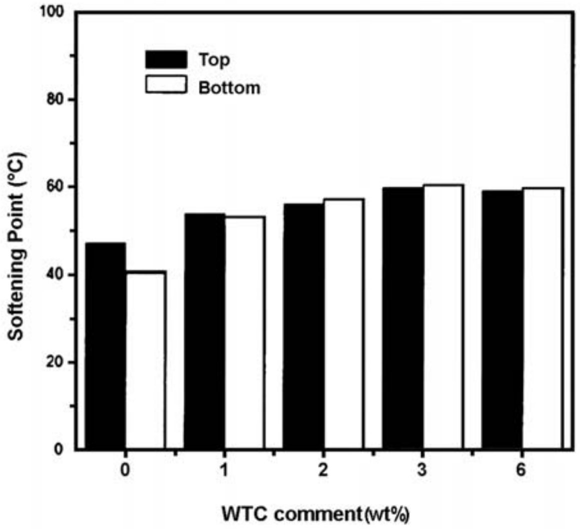

Figure 2. Effect of WTC contents on storage stability of the WTC modified asphalts.

niques makes a direct approach to the compatibility of WTC and SBR/WTC modified asphalts. The morphologies of WTC and SBR/WTC modified asphalts are shown in Figure 3.

Figures 3a and 3b show the TEM images of 1 and 2 wt% of WTC modified asphalt samples. WTC grains dispersed irregularly in asphalt. There was no visible difference in the bonding of the binder between 1 wt% WTC and the 2 wt% WTC modified asphalts. When the content of WTC fixed at 3 wt%, WTC grains dispersed relatively uniform in the asphalt (Figure 3c). The diameter of WTC grains is

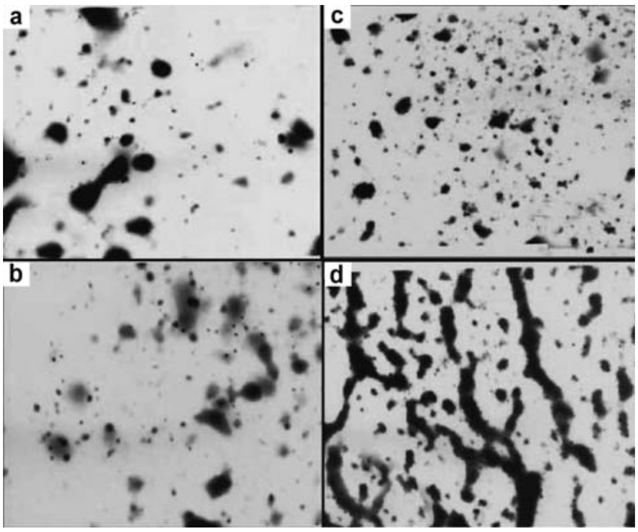

Figure 3. TEM Images of WTC modified asphalt: (a) 1% WTC modified asphalt, (b) 2% WTC modified asphalt, (c) 3% WTC modified asphalt, and (d) 5% WTC modified asphalt.

the minimum of 9 nm and maximum of 0.83 μm in the WTC modified asphalt with WTC content of 3 wt%. This suggestes that asphalt bonded better with the WTC grains. The weathering of coal not only tended to alter it chemically but also to disintegrate or weaken it physically. Generally, when WTC is mixed with base asphalt, the surface voids of WTC were filled with asphalt. If the rate of loss of moisture from the surface was faster than the interior moisture reduction, then the shrinkage at the surface of the lump coal would be greater than in the interior. Hence stresses were generated, cracks may have been developed on the coal surface and the strength of coal may have decreased. During the period that the coal was exposed, the repeated changes in humidity and temperature, which create stress and strain within the lumps, increased the rate of friability. Higher friability of coal produced higher percentage of fines [25]. The fine grains of WTC with high surface energy had the ability to attach to the substance in asphaltenes, resulted in some changes of the chemical composition of WTC modified asphalt.

The physical properties may be changed significantly in modified asphalt compared to base asphalt. This was in accordance with the result shown in Table 1. When the content of WTC was 5 wt%, the WTC grains, however, were clumped together and the asphalt could not penetrate into a bulky aggregate of coarse particle structure (Figure 3d). It was known that in the process of asphalt modification, the structure and the properties of modified asphalt were of vital importance. Therefore, the content of additive seems to be one of the key factors.

The shape of asphalt, surface texture and WTC distribution in modified asphalt could be observed and analyzed by scanning electron microscopy micrographes and compared with those of base asphalt. The typical morphology of base asphalt with SEM is shown in Figure 4a. As the content of WTC increased up to 3 %, the modified asphalt was obtained with relative uniformity as shown in Figure 4b. However, when the content of WTC was 5%, a large number of polymer “islands” were noticed, indicating an incompatibility between WTC and asphalt. This was in accordance with the result of TEM.

With the addition of SBR, the relative uniformities are shown in Figures 4d-4f in which the dark area in the modified asphalt demonstrates homogeneous

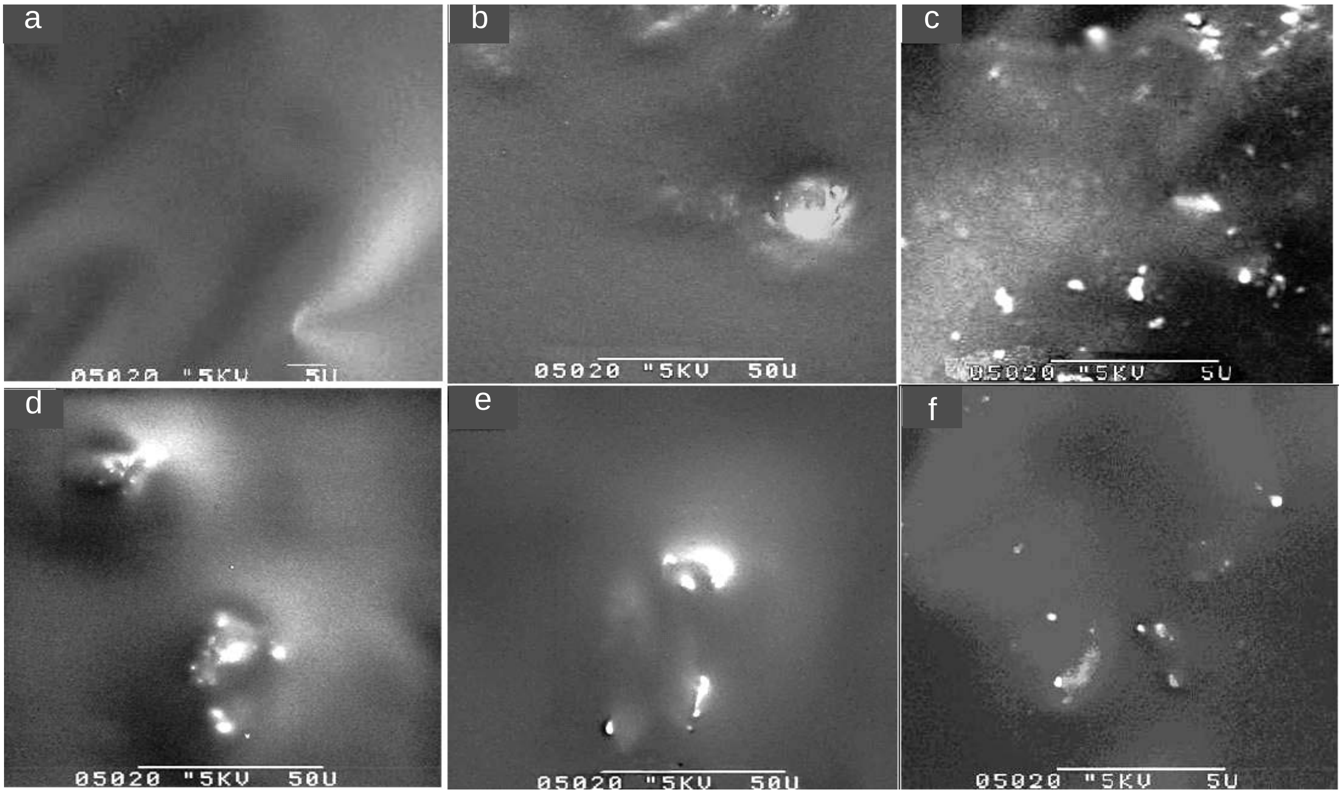

Figure 4. SEM Micrographes of: (a) base asphalt, (b) 3% WTC modified asphalt, (c) 5 wt% WTC modified asphalt, (d) 2 wt% SBR/3% WTC modified asphalt, (e) 3 wt% SBR/3% WTC modified asphalt, and (f) 3 wt%SBR/4%WTC modified asphalt.

phase composition. No significant changes were found with the increasing content of SBR in SBR/WTC modified asphalt. The morphology of the polymer "islands" were different from the asphalt modified with 5 wt% of WTC and indicated the improvement of incompatibility. However, the brighter regions distributed in the modified asphalt, indicate that there are WTC particles always incompatible with asphalt despite the increased content of SBR.

As we know, the main composition in WTC is humic acid (the content of humic acid was obtained 60 wt% of WTC, in our lab). Humic acid was a high molecular weight macromolecule consisting of complex polymeric aromatic structures [26]. In fact, the interactions between WTC and asphalt were occurred mainly due to the presence of humic acid. It was inevitable that the impurity in WTC affected the compatibility between WTC and asphalt. The impurity distributed was incompatible with the modified asphalt resulted in the formation of the brighter region. Therefore, the influence of purified WTC on modified asphalt was necessary to be studied in the near future.

FTIR Analysis

The observed differences in the WTC and SBR/WTC modified asphalts should be attributed to the structural variations. The main structural modifications that take place (during the addition of WTC or SBR/WTC) in modified asphalts were the chemical reactions between polymer and asphalt. The differences in properties of base asphalt and WTC modified asphalt before and after the addition of SBR imply the changes in their chemical structure. In order to study the asphalt aging, the chemical reactions were studied through FTIR analysis. The results of the modified asphalts were compared with base asphalt.

Figure 5 shows the infrared spectra of WTC modified asphalt before and after the applications of SBR. A similarity between WTC and SBR modified asphalt is evident. The bands at 870 cm^{-1} correspond to $\delta_{C\text{-}H}$ aromatic and the ones at 1216 cm^{-1} correspond to the aromatization and esterification in WTC and

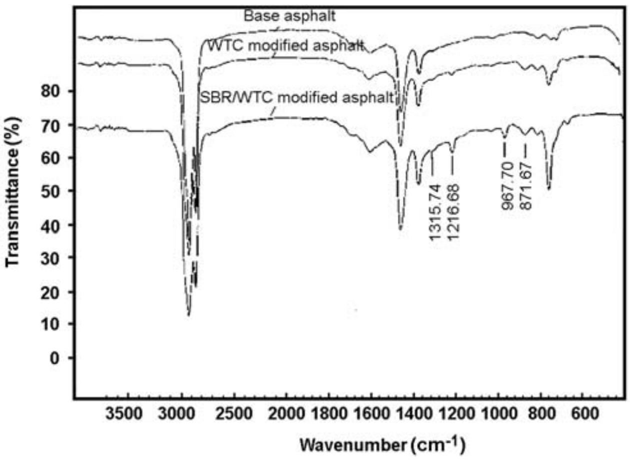

Figure 5. FTIR Analyses of WTC and SBR/WTC modified asphalts.

SBR/WTC modified asphalt samples. New bands at 1315 cm^{-1} and 965 cm^{-1} correspond to bending C-H of trans-disubstituted –CH=CH= modes of vibration and δ_{C-H} aromatic compounds, respectively in SBR/WTC modified asphalt sample. The promotion of aromatic compounds in modified asphalt indicates the improvement of the compatibility between modifier and asphalt. However, there are weak peak areas that show chemical reaction was not the main change due to modification.

CONCLUSION

The physical properties of WTC and SBR/WTC modified asphalts, including softening point, penetration, and ductility before and after RTFOT aging were characterized. The softening point increased significantly and the low temperature (5°C) ductility changed little when SBR was absent at the WTC content of 3 wt% in the modified asphalt. The storage stability could be effectively improved through the appearance of WTC. TEM data showed WTC grains with the diameter of the minimum of 9 nm and maximum of 0.83 μm are dispersed relatively uniform in WTC modified asphalt. While SEM micrograph of WTC modified asphalts showes a relatively homogeneous and “islands” phases, especially when WTC content was 3 wt%. This suggestes that asphalt bonded better with the WTC grains.

SBR had marked effect on the low temperature (5°C) properties and improved the aging resistance with increasing SBR content up to 4 wt%. Therefore, SBR/WTC modified asphalts had the improved properties of increasing softening points, promoting ductility, and aging resistance. However, as the brighter regions distributed in the modified asphalt, indicates that there were WTC particles always incompatible with asphalt despite the increased content of SBR. That might be due to the impurities in WTC that affectes the compatibility between WTC and asphalt. The FTIR analysis showed new weak peak areas in modified asphalts indicating that physical alterations were the main changes in modified asphalts.

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