



Study on Preparation Method of Terminal Blend Rubberized Asphalt Binder

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Terminal Blend (TB) asphalt rubber is prepared by being sheared with high speed for a long time a high temperature and has good low temperature performance and anti-fatigue performance. But due to the aging of asphalt and desulfurization and degradation of crumb rubber, the high temperature performance of TB is not ideal. In order to propose an effective way to solve this problem and improve the high temperature performance, a series of TB-B and TB-C asphalt were prepared with crumb rubber by changing dosage and preparation temperature in nitrogen environment and soluble crumb rubber in atmospheric environment, respectively. As a comparison group, TB-A asphalt was prepared using crumb rubber under atmospheric environment. Dynamic shear rheometer (DSR) and binding beam rheometer (BBR) were used to investigate the rheological characteristics, polymer segregation experiment was performed to evaluate the storage stability, and Fourier Transform Infrared (FTIR) spectroscopy and thermogravimetric analysis were carried out to explore the aging degree of asphalt. TB-A had good storage stability but was brittle due to serious asphalt aging during preparation, and its high and low temperature performance were not good. The introduction of nitrogen could effectively decline aging degree and guaranteed TB-B best comprehensive performance among these three kinds of modified asphalt. Soluble crumb rubber was obtained by pretreating crumb rubber and making it desulfurize and degrade, which reduced the preparation and consequently inhibit the occurrence of aging. The high and low temperature properties of TB-C met specification, but storage stability was not insufficient when crumb rubber content was more than 15%. Overall, both preparation in nitrogen environment with conventional crumb rubber and preparation in atmospheric environment with soluble crumb rubber can effectively alleviate the aging degree of TB asphalt.

Keywords: crumb rubber modified asphalt, terminal blend, preparation process, asphalt aging, rubber powder degradation, rheology

INTRODUCTION

With the rapid development of automobile possession, the amount of waste tires has proliferated. The traditional disposal methods of waste tires, such as incineration, landfill and piling up not only occupy a lot of land resources but also easily breed mosquitoes and cause fires (Xie et al., 2019; Yan et al., 2020). Waste tires can be ground at normal temperature or in liquid nitrogen to obtain rubber powder, which has been proved to be can effective modifier

to asphalt. The emergence of asphalt rubber provides an environmentally friendly way to waste tires (Yang et al., 2017; Nanjegowda and Biligiri, 2020; Wang et al., 2020). So far, asphalt rubber has been developed for many years and widely used in the United States, South Africa and some other countries. However, asphalt rubber prepared with typical wet process has poor storage stability and high viscosity. It requires special stirring equipment to avoid segregation and can only be used in short time, which hinders its promotion and application (Zhou et al., 2014; Hosseinneshad et al., 2019; Pouranian et al., 2020). Based on this, an alternative rubber modified asphalt known as Terminal Blend rubberized asphalt binder (TB asphalt) has attracted increasing concerns since the 1980s. Unlike rubber modified asphalt produced through traditional wet process, TB asphalt is generally prepared with less crumb rubber content under higher shear temperature and has the characteristics of low viscosity, good storage stability, and thus has good application prospects (Lo Presti et al., 2012; Lo Presti, 2013; Zeinali et al., 2014; Han et al., 2016).

Similar to polymer modified asphalt, TB asphalt can be produced directly in asphalt plants. The characteristics of processing technology includes high temperature (200~300°C), high pressure (> 1 atm) and high shear speed (3000~8000 r/min) (Han et al., 2016; Wen et al., 2021). Under such strict preparation conditions, the swelling of rubber powder in typical wet is replaced by the desulfurization and depolymerization of rubber, and smooth and uniform binder is obtained (Ghavibazoo and Abdelrahman, 2014). Compared with asphalt rubber, TB asphalt has better low temperature performance, fatigue performance, storage stability, anti-aging performance and workable performance (Han et al., 2017; Lin et al., 2017). The University of California, Berkeley and the Federal Highway Administration took accelerated pavement test via heavy vehicle simulators (HVS) and found that TB asphalt had better fatigue performance than asphalt rubber and was suitable for dense graded mixture (Qi et al., 2006; Santucci, 2009; Tang et al., 2017). Lin found that during the preparation of TB asphalt, light components such as aliphatic generated because of the desulfurization and degradation of rubber powder, which increased the low temperature properties of TB asphalt (Lin et al., 2018). Abdelrahman found that with the rise of interaction temperature and the extension of interaction time, the diffusion rate and degradation rate of rubber powder in the asphalt was promoted, thereby the storage stability was improved (Ghavibazoo and Abdelrahman, 2013). Tang used rolling thin film oven test (RTFO) and pressure aging vessel test (PAV) to investigate the aging performance of TB asphalt, and found that TB asphalt had better anti-aging performance than base asphalt (Tang et al., 2019). However, the desulfurization and degradation of TB rubber powder under high temperature conditions break the cross link bonds and damage the network structure of the system, which leads to the greatly loss of viscosity and elasticity and the deterioration of high temperature performance (Tang et al., 2016). In previous studies, the ways to improve high-temperature performance of TB asphalt can be divided into two categories. One is to optimize the preparation process (Ragab and Abdelrahman, 2014). Ragab et al. (2013) pointed out that

the degradation degree of rubber powder could be decreased by strictly controlling the preparation temperature. The crumb rubber can form three-dimensional network structure with the asphalt through adjusting the preparation process, which endue TB asphalt with both storage stability and high temperature performance (Ragab and Abdelrahman, 2014). However, it is not universal to improve the high temperature performance of TB asphalt via preparation process because the types of crumb rubber and asphalt may also be different (Ragab et al., 2015; Ghavibazoo et al., 2016). Wu increased the amount of crumb rubber in the asphalt and added a cross-linking agent to prepare TB asphalt with high viscosity and high storage stability. Compared with SBS modified asphalt, it was found that TB asphalt had better high temperature performance and lower temperature performance (Wu et al., 2013). The other is compound modification of TB asphalt. SBS (styrene-butadiene-styrene block copolymers), PPA (polyphosphoric acid), rock asphalt and nano-materials are commonly used compound modifier. Jin, Greene and Lin used SBS to modify TB asphalt, and they found that the addition of SBS was beneficial to the remodeling of the cross-linked network in TB asphalt, and then improved the high temperature performance without degrading the low temperature performance (Jan et al., 2014; Greene et al., 2015; Lin et al., 2018). Lin's research found that although the addition of PPA helped to improve the high temperature performance of TB asphalt, but it had negative impact on the cross-linking network in the asphalt, which in turn adversely affected the low temperature performance (Lin et al., 2017, 2018). Huang used rock asphalt to modify TB asphalt and carried out a series of experiments. The results showed that rock asphalt increased the high temperature performance of TB asphalt, but slightly decreased the low temperature performance (Huang et al., 2016). Han used modified TB asphalt with nano-silica and found that the rutting resistance of TB asphalt at high temperature was improved, but the crack resistance at low temperature was slightly reduced (Han et al., 2017). You added amorphous-poly-alpha-olefin (APAO) additives into TB asphalt and found that APAO enhanced the elastic components of asphalt, which increased both high and low temperature performance of TB asphalt (You et al., 2019).

At present, the performance of TB asphalt prepared by different asphalt plants varies enormously and there is no uniform specification (Xiao et al., 2015). Meanwhile, the existing studies generally focus on the properties of TB asphalt, and the specific research about the preparation method is relatively few. Normally, TB asphalt is prepared at high temperature (more than 200°C), which results in the rapid volatilization of light components in asphalt and the thermal-oxidative aging of asphalt (Zanzotto and Kennepohl, 1996). In asphalt plants, sealed oxygen-barrier asphalt tanks can ensure that TB asphalt is not aging under high temperature and pressure production conditions, but it is not easy to create such conditions in the laboratory. Huang proposed two different preparation methods to alleviate the aging phenomenon in the preparation of TB asphalt (Lv et al., 2019).

- (1) The temperature was reduced to 220°C, and the reaction time was extended to more than 10 h.
- (2) The crumb rubber was pretreated through desulfurization and depolymerization before being added to asphalt which reduced the interaction temperature and time of preparation.

However, the longer reaction time in Method 1 seriously affected the production efficiency, and did not play a positive role in preventing aging. The pretreatment of the crumb rubber in Method 2 required various auxiliary materials and the procedures were more complicated. Billiter et al. (1997) explored the preparation of asphalt rubber at high temperature and found that when the interaction temperature was 232~260°C, nitrogen could be used to create an oxygen-barrier environment. To prevent the asphalt from aging at high temperature, Zanzotto prepared the asphalt rubber in two steps. First, the asphalt rubber was thermally depolymerized in an autoclave, and then the rubber and asphalt were mixed at 170~180°C. But the two steps needed to be carried out continuously, which increased difficulty of operation (Zanzotto and Kennepohl, 1996).

To explore a simple and feasible method to reduce asphalt aging during the preparation process, this paper proposes two preparation methods and compares them with TB asphalt prepared in atmospheric environment. As shown below:

- (1) As a comparison group, TB-A asphalt was prepared using crumb rubber in atmospheric environment.
- (2) Crumb rubber was added to base asphalt under the protection of nitrogen to prepare TB-B asphalt through a self-developed nitrogen protection device.
- (3) TB-C asphalt was prepared using soluble crumb rubber at low temperature (<200°C).

The effect of processing technological parameters (such as rubber powder content and shearing temperature) on the physical properties of TB asphalt was investigated. To compare the rheological performance of TB asphalt prepared with different methods, dynamic shear rheology experiment was carried out. Meanwhile, bending beam rheometer was used to study the low temperature property of TB asphalt. Specially, the storage stability of TB asphalt was analyzed via polymer isolation experiment. Last but not least, the aging degree of asphalt during the preparation process was characterized with Fourier Transform Infrared spectrometer (FTIR), and its microscopic mechanism on TB asphalt was explored by thermogravimetric analyzer (TG).

MATERIALS AND METHODS

Materials

Base asphalt binder of grade 70 was supplied by Hunan Poly Company (Hunan, China). 80 mesh crumb rubber was purchased from Sichuan Lubaotong Company (Chengdu, China). The low Mooney soluble crumb rubber (Mooney viscosity 30, sol content 62.6%) was provided by Professor Shifeng Wang from

Shanghai Jiao Tong University. The technical parameters are shown in Tables 1, 2.

Preparation of TB Asphalt

In this study, 5, 10, 15, 20, and 25% of crumb rubber were added to base asphalt under atmospheric and nitrogen environments, respectively. The mixture was then swelled in an oven at 180°C for 30 min. At last, the binder was mixed by high-speed shear instrument at a rate of 4000 r/min for 3 h at 220, 240, and 260°C. The modified asphalt prepared under atmospheric environment was recorded as TB-A, and the modified asphalt prepared under nitrogen environment was recorded as TB-B. It should be noted that after mixing the binder in nitrogen environment, it is necessary to continuously pass nitrogen until the temperature decrease to about 160°C. The nitrogen protection device was made by our laboratory, and the schematic diagram is shown in Figure 1. The device is hermetically sealed and nitrogen was introduced through nozzle. Similarly, to prepare TB-C, the soluble crumb rubber with the same content was added to base asphalt and then swelled in an oven at 180°C for 30 min, followed by being mixed with a high-speed shear instrument at 160, 180, and 200°C at a rate of 4000 r/min for 1 h.

Test Methods

The penetration (25°C) and softening point of the TB asphalt were tested using the PNR 12 penetration meter and RKA 5 softening point meter (Antongpa, Austria). The digital ductility tester (Infra Test, Germany) was used to measure the ductility of the binder at 15°C and the tensile speed was 50 mm/min.

According to the JTG-T0628-2011 test method, the dynamic shear rheometer (DSR, MCR 302, Antongpa, Graz, Austria) was used to test the complex shear modulus and phase angle of the

TABLE 1 | Properties of base asphalt binder.

Item	Units	Test Results	Standard
Penetration (25°C, 5 s, 100 g)	0.1 mm	69	JTG E20-2011 T0604-2011
Softening temperature	°C	46.5	JTG E20-2011 T0606-2011
Ductility (15°C)	cm	>150	JTG E20-2011 T0605-2011
Solubility	%	99.87	JTG E20-2011 T0607-2011
Density (15°C)	g/cm ³	1.039	JTG E20-2011 T0603-2011
RTFO treated at 163°C for 85 min			
Quality change	%	-0.024	JTG E20-2011 T0609-2011
Residual penetration ratio	%	61.7	JTG E20-2011 T0604-2011
Residual ductility (10°C)	cm	6.3	JTG E20-2011 T0605-2011

TABLE 2 | Properties of crumb rubber.

Item	Result	Standard
Water content (%)	0.96	HG/TXXX-2001 7.2.2
Ash content (%)	9.0	GB4498
Acetone extract content (%)	13.6	GB/T3516
Density (g/cm ³)	0.96	GB/T533
Tensile strength (MPa)	6.2	GB/T528
Elongation at break (%)	850	GB/T52

binder. The rheological tests were carried out by parallel plates with a diameter of 25 mm and a spacing of 1 mm under strain controlling mode ($\omega = 10 \text{ rad/s}$).

According to the JTG-T0627-2011 test method, the bending creep stiffness and creep rate (m -value) of asphalt were measured using a bending beam rheometer (BBR, TE-BBR, Cannon, Tokyo, Japan). A contact load of 35 mN was applied to the rectangular asphalt samples ($125 \text{ mm} \times 12.7 \text{ mm} \times 6.35 \text{ mm}$) prepared in advance at -12°C and -18°C .

The storage stability of TB asphalt was tested according to the polymer isolation experiment of JTGT 0661-2011. The standard sample tube (about 25 mm in diameter and about 140 mm in length) filled with the asphalt sample was left in an oven at 163°C for 48 h, then was placed in the freezer for more than 4 h and cut into three sections. Finally, the softening points of the top and bottom samples were measured to determine the softening point difference.

According to the JTG-T0625-2011 test method, the viscosity of TB-A, TB-B, TB-C at 177°C was measured using a Brookfield rotary viscometer.

Fourier Transform Infrared (FTIR) spectroscopy (Thermo Fisher, Waltham, MA, United States) was used to characterize

the chemical structure of TB-A, TB-B, and TB-C. The spectrum ranged from 4000 to 500 cm^{-1} , and scanning was repeated 32 times.

Thermal analysis of TB asphalt was performed by Thermogravimetry analyzer (TGA STA449F5, Netzsch, Germany) in a nitrogen atmosphere. About $10 \pm 0.1 \text{ mg}$ sample was heated from 50 to 700°C in the furnace with a constant heating rate of 10°C/min .

RESULTS AND DISCUSSION

Physical Properties

Penetration, softening point, and ductility are common indicators of the high and low temperature performance of asphalt. Studies show that the physical properties of TB asphalt are close to those of base asphalt (Huang et al., 2016). Therefore, the authors tested the physical properties of TB-A, TB-B, and TB-C, and compared and analyzed them with base asphalt.

It can be seen from **Figure 2** and **Table 3** that compared to base asphalt, TB-A asphalt has lower penetration and much

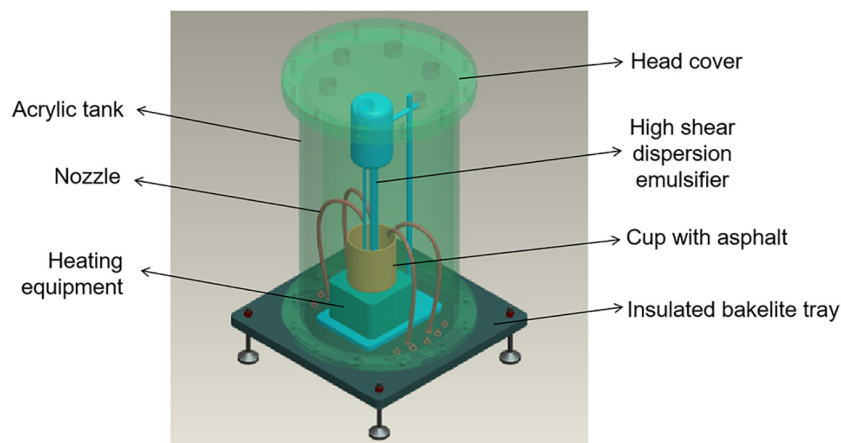


FIGURE 1 | Schematic diagram of nitrogen environment box.

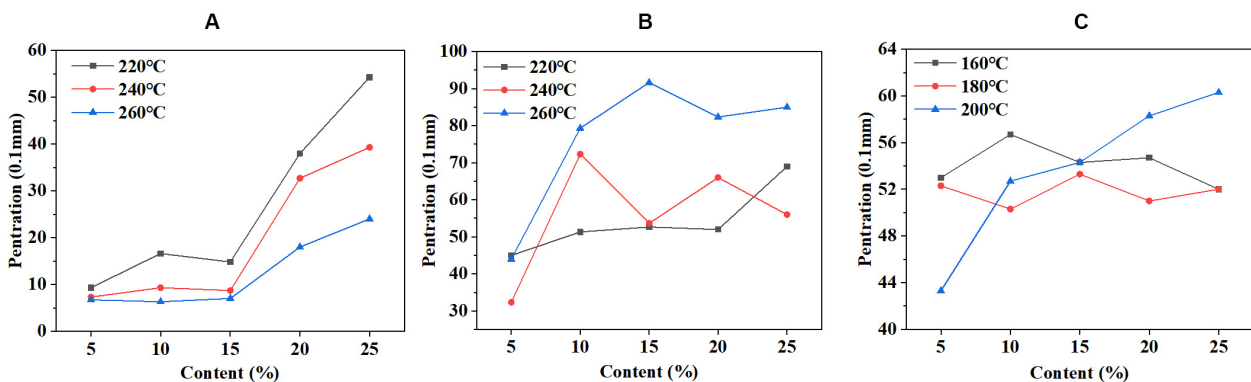


FIGURE 2 | Penetration test results of TB asphalt. (A) TB-A. (B) TB-B. (C) TB-C.

TABLE 3 | Softening point and Ductility test results of TB asphalt.

CR content Sample ID	TB-A			TB-B			TB-C		
	220°C	240°C	260°C	220°C	240°C	260°C	160°C	180°C	200°C
	Softening point (°C)								
5%	—	—	—	38.0	55.3	47.1	50.5	51.1	53.7
10%	70.2	—	—	49.8	47.8	47.7	50.5	52.3	51.9
15%	74.8	—	—	52.8	51.4	46.1	52.2	52.6	54.0
20%	55.5	67.5	72.4	56.1	51.6	47.6	53.3	56.5	53.8
25%	56.0	56.3	58.8	51.6	52.8	45.4	56.9	57.0	55.0
	Ductility (cm)								
5%	0.3	0.29	0.3	22.3	12.9	17.6	21.8	16.1	10
10%	0.61	0.31	0.28	28.4	34.3	84	20.2	17.5	10.7
15%	0.63	0.31	0.73	23.7	21	> 100	12.1	9.9	9.8
20%	13.7	11.6	0.91	20.1	29	81.3	10.2	10.3	11.3
25%	56.6	12.3	1.2	20.5	20.4	78.2	10.4	8.6	11.1

“—” means that the softening point test temperature is greater than 80°C, and it is necessary to switch to glycerin for heating. Considering that the softening point of TB asphalt is not so high, it means that the requirements of TB asphalt are not met, so the test was not performed.

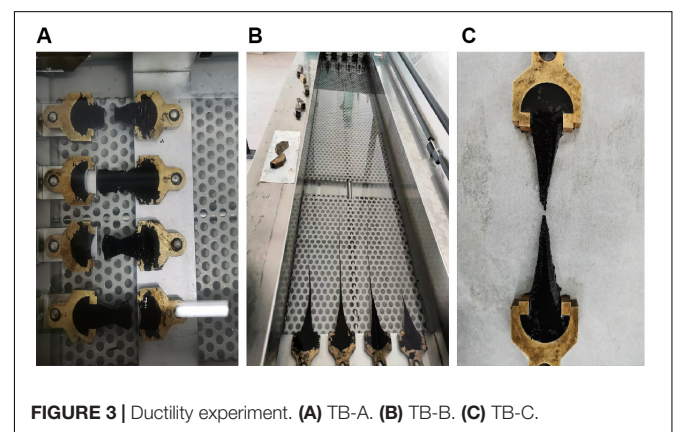
higher softening point. This is because at high temperatures, the light components in asphalt is excessively volatilized and the thermal oxygen aging of the binder occurs, which increases the asphaltene content and makes the asphalt become hard and brittle, and the higher the preparation temperature, the more obvious this phenomenon. In addition, with the increase of crumb rubber content, the penetration improves and the softening point declines as a whole, which may be related to the anti-aging agent contained in the crumb rubber.

There are two important reactions during the preparation process of TB asphalt, one is the aging of base asphalt, the other is the desulfurization and degradation of the crumb rubber. When the former dominates, TB asphalt obtained is hard and brittle, and vice versa. Compared with TB-A asphalt, the penetration and softening point of TB-B asphalt is closer to base asphalt, which means the protection of nitrogen during the preparation process has a positive effect on preventing TB asphalt from aging and the later reaction dominates. Meanwhile, the penetration of TB-B increases and the softening point decreases with preparation temperature. When the preparation temperature reaches 260°C and the crumb rubber content exceeds 10%, the penetration and softening point of TB-B tend to be stable. But the regularity of penetration changes with the amount of rubber powder is not obvious, which is consistent with some studies in the literature. With the increment of crumb rubber content, the penetration of TB asphalt decreased according to Wei and Song's research (Wei, 2016; Song, 2017), but increase in the studies of Huang et al. (2016), which indicates that the influence of crumb rubber on the penetration of TB asphalt is very complicated.

The softening point of TB-C asphalt increases with the soluble crumb rubber content and the preparation temperature. But the penetration of TB-C has different variation trend with soluble crumb rubber content at different preparation temperature. It is not significantly affected by crumb rubber content at 160 and 180°C. However, when the temperature increases to 200°C,

the penetration increases with the amount of soluble crumb rubber remarkably, which indicates that at 200°C the aging of base asphalt dominates. In addition, over the entire temperature range, the penetration of TB-C asphalt is lower than base asphalt, which may be due to that the crumb rubber swells and dissolves in asphalt and increases the viscosity of the asphalt.

Ductility is an indicator of the low-temperature plasticity of asphalt and closely related to the low-temperature performance. It was found in the test that the TB-A asphalt was very brittle, and easily broke at 15°C, as shown in **Figure 3A**. So the serious aging of TB-A asphalt prepared under atmospheric environment is confirmed again. As can be seen from **Table 3**, TB-B has the best low temperature ductility followed by TB-B, and TB-A has the worst. Besides, the ductility of TB-B asphalt is influenced greatly by preparation and reaches to the maximum at 260°C, much higher than the TB-B asphalt prepared at other temperature (**Figure 3B**). Its However, as shown in **Figure 3C**, the ductility of TB-C asphalt is smaller than TB-B asphalt. The reason could be that the crumb rubber in TB-C asphalt does not completely dissolve, so the system is not heterogeneous.

**FIGURE 3** | Ductility experiment. (A) TB-A. (B) TB-B. (C) TB-C.

High Temperature Rheological Properties

In this section, the effects of crumb rubber content and preparation conditions on complex modulus (G^*), phase angle (δ) and rutting coefficient ($G^*/\sin\delta$) are analyzed. Complex modulus G^* is the ratio of maximum shear stress to maximum shear strain and characterizes the ability of the asphalt to resist deformation under repeated shear stress. Phase angle δ is the time lag of the applied stress and the resulting strain, which reflects the viscoelasticity of the asphalt (Jin et al., 2019; Wang and Ye, 2020).

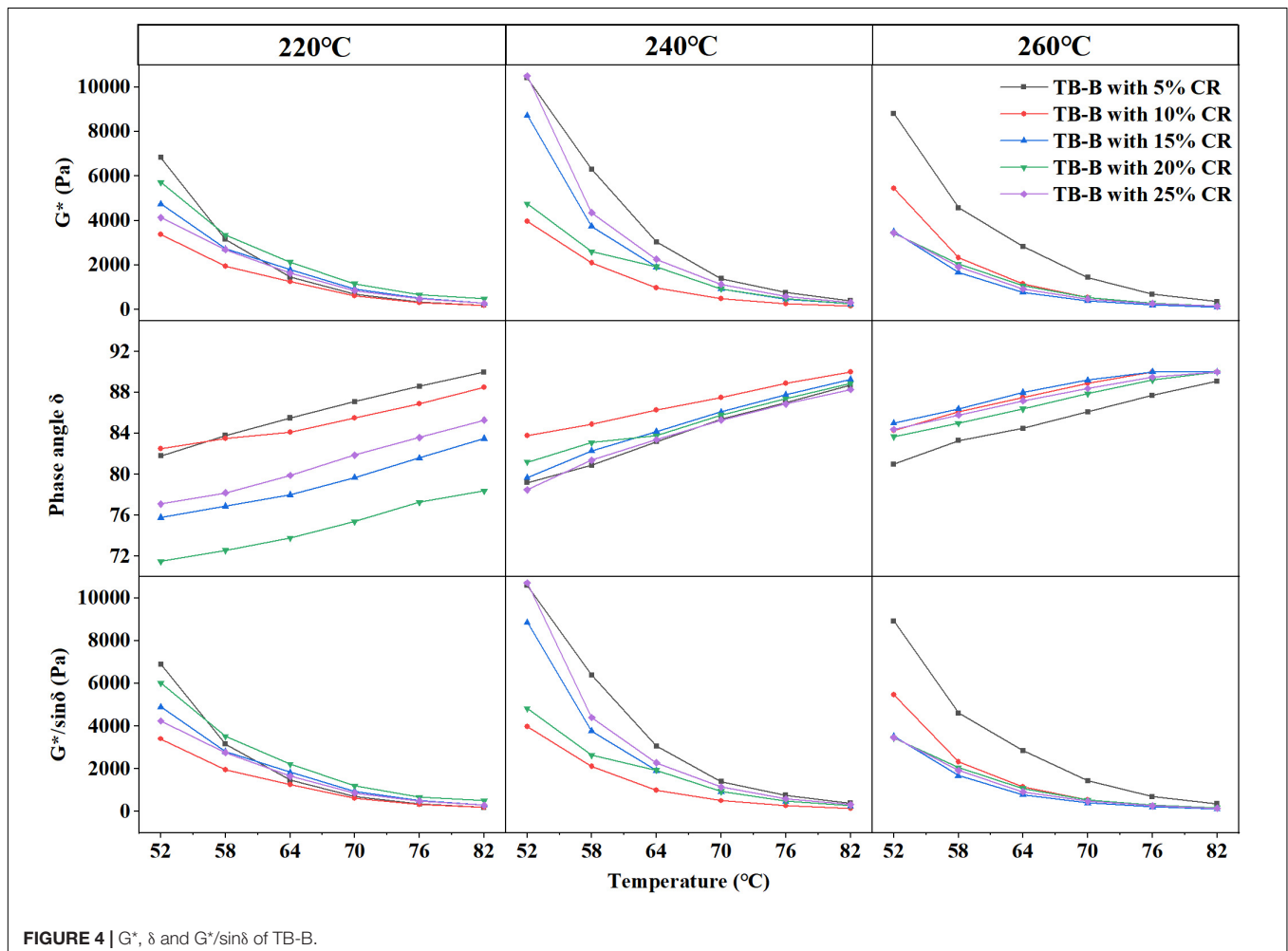
As shown in Figures 4, 5, TB-B has smaller G^* and $G^*/\sin\delta$ but greater δ than TB-C, which indicates that the elastic ratio of TB-B is lower than TB-C and the anti-deformability at high temperature of TB-B is worse. This phenomenon is resulted from the desulfurization and degradation of crumb rubber at high temperature and high-speed shear rate, which causes elastic losses results in the reduction of the deformation resistance and viscoelastic properties of the binder.

From Figure 5 one can see that the G^* of TB-C asphalt increases and the phase angle δ decreases with increment of

crumb rubber, which means that the increment of soluble crumb rubber helps improve the anti-deformability and elasticity of the modified asphalt. This is similar to rubber modified asphalt prepared by traditional wet process, which shows that the interaction mechanism between soluble crumb rubber and base asphalt is mainly swelling. In addition, G^* , δ , and $G^*/\sin\delta$ of TB-C asphalt decreases when improve preparation temperature, which can be attributed to the aging of asphalt.

Low Temperature Creep Properties

The bending beam rheometer (BBR) test is often used to evaluate low temperature creep properties of asphalt, and two parameters—creep stiffness S and creep rate m can be obtained from this test. S represents the toughness of asphalt under low temperature conditions, the larger the S value, the more brittle the asphalt material and the easier the road surface to crack. Creep rate m reflects the stress relaxation ability of asphalt at low temperature, the larger the m value, the better the stress relaxation ability of the asphalt material, and the lower the possibility of low temperature cracking. The BBR tests of TB asphalt prepared in this study were



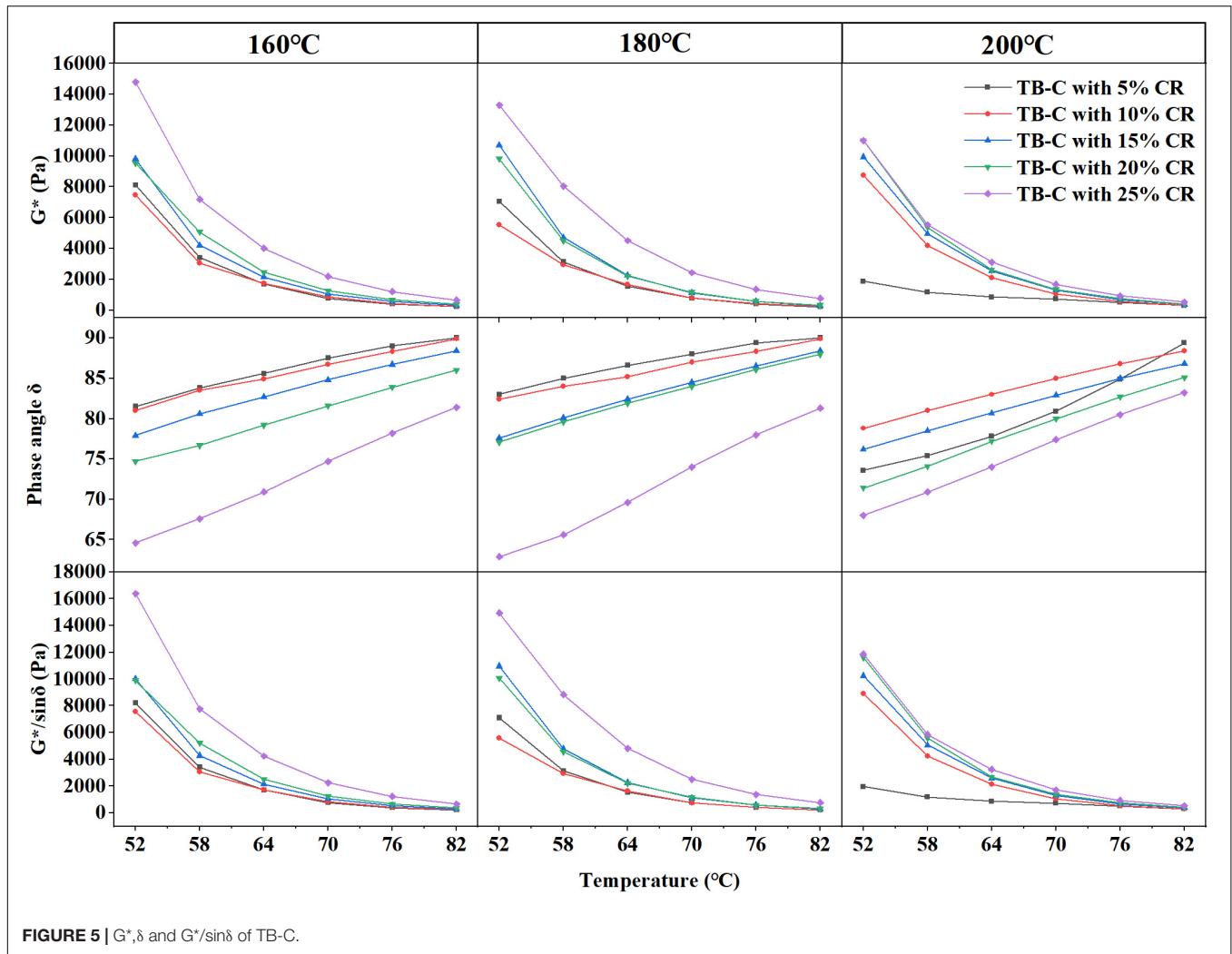


FIGURE 5 | G^* , δ and $G^*/\sin\delta$ of TB-C.

performed under a stress of 100 g (980 mN) for 240 s (Li et al., 2017).

According to Superpave binder grade specifications, at the lowest design temperature the creep stiffness of asphalt loaded for 60 s should be less than 300 MPa, and m -value should be greater than 0.3. As shown in Figure 6, when the crumb rubber content is less than 15%, the creep stiffness and creep rate of TB-A asphalt at -12°C and -18°C do not meet the requirements of the specification, indicating that the low temperature grade of TB-A asphalt is higher than -12°C . Besides, the creep stiffness of TB-A asphalt gradually increases and m -value gradually decreases when preparation temperature goes up. This means that when temperature is higher than 220°C , TB-A asphalt ages seriously. Further increase of temperature will exacerbate this phenomenon.

From Figure 7 it can be found that at the same temperature, increasing content of crumb rubber decreases the creep stiffness and increases the m -value of TB-B asphalt. This is ascribed to that aliphatic small molecules generated from the desulfurization and

depolymerization of crumb rubber improves low temperature toughness and stress relaxation ability of the binder.

Figure 8 shows the creep stiffness and m -value of TB-C asphalt. At the same temperature the creep stiffness of TB-C asphalt decreases and creep rate does not change much as the soluble crumb rubber content increases. As temperature increases, the influence of the rubber powder content on S and m declines.

From the above analysis we can draw such a conclusion that at the same test temperature, TB-A has the largest S , followed by TB-C and finally TB-B, but the order of m values is just the opposite. Thus TB-B has the best low temperature rheological performance, followed by TB-C, finally TB-A.

Storage Stability

Due to the big difference of molecular weight, density and solubility parameters between rubber powder and asphalt, the storage stability of asphalt rubber prepared through traditional wet process is usually poor, which is a key issue restricting the development of rubber asphalt (Lin et al., 2018). According to the specification, to avoid segregation the softening

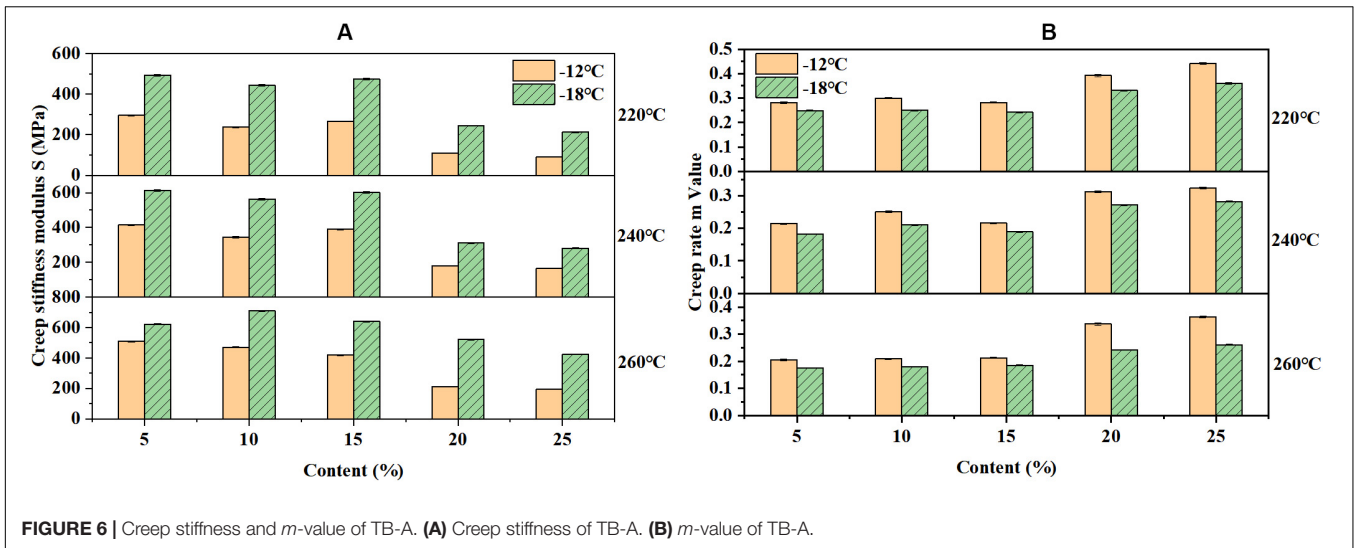


FIGURE 6 | Creep stiffness and *m*-value of TB-A. (A) Creep stiffness of TB-A. (B) *m*-value of TB-A.

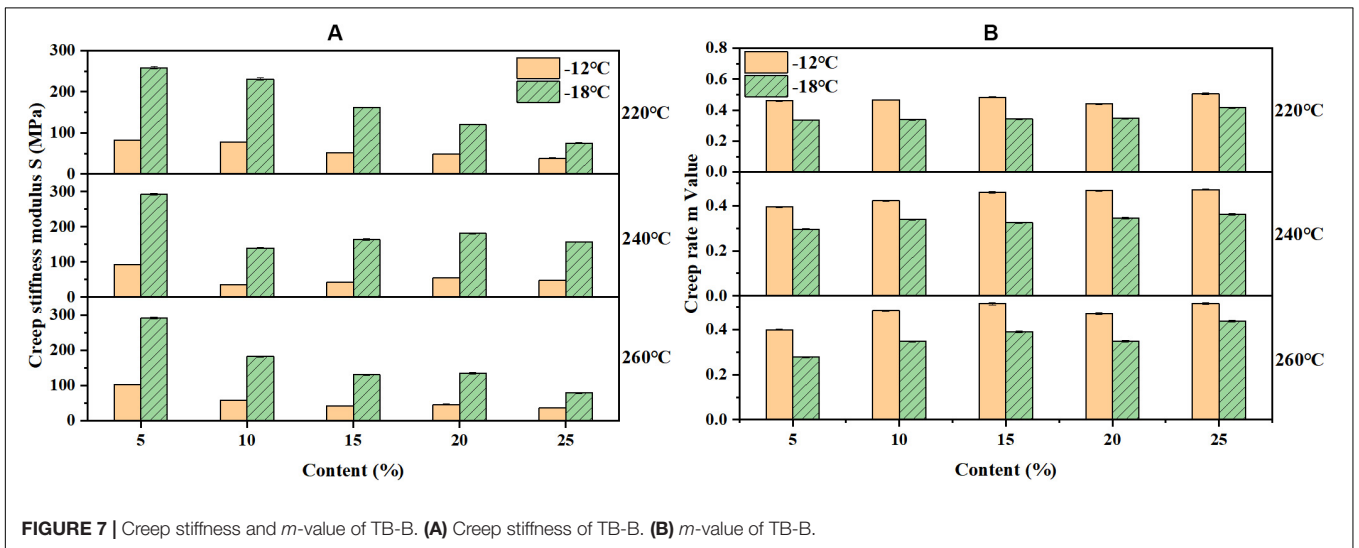


FIGURE 7 | Creep stiffness and *m*-value of TB-B. (A) Creep stiffness of TB-B. (B) *m*-value of TB-B.

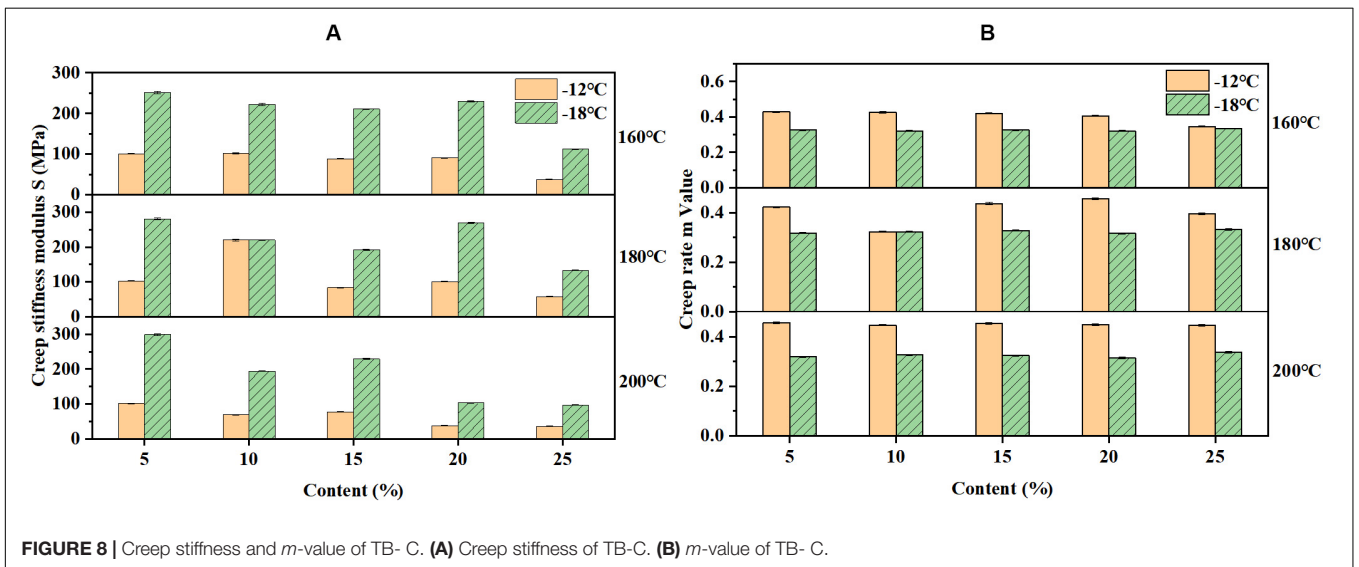


FIGURE 8 | Creep stiffness and *m*-value of TB-C. (A) Creep stiffness of TB-C. (B) *m*-value of TB-C.

TABLE 4 | Softening point difference of TB asphalt (°C).

CR content Sample ID	TB-A			TB-B			TB-C		
	220°C	240°C	260°C	220°C	240°C	260°C	160°C	180°C	200°C
5%	—	—	—	0.7	0.05	0.15	0.5	0.95	0.85
10%	0.05	—	—	1.05	0.75	0	1.65	0.4	1.7
15%	0.3	—	—	0.8	2.2	0.1	0.1	0	4.6
20%	0.4	1	0.75	2.75	0	0.85	6.95	4.85	10.35
25%	0.2	0.8	0.55	0.15	1.25	0.55	9.75	11.15	11.8

“—” means that the softening point test temperature is greater than 80°C, and it is necessary to switch to glycerin for heating. Considering that the softening point of TB asphalt is not so high, it means that the requirements of TB asphalt are not met, so the test was not performed.

point difference of polymer modified asphalt after being stored for 48 h at high temperature should be less than 2.5°C. As an important performance evaluation index of modified asphalt, the storage stability of three types of TB asphalt prepared in this study was measured with polymer isolation experiment.

It can be seen from **Table 4** that the softening point difference of TB-A and TB-B are less than 2.5°C, but most samples of TB-C asphalt do not meet the specification. Also, an increase in the content of crumb rubber in the asphalt leads to an increase in the softening point difference. The lowering of the interaction temperature will aggravate the segregation of modified asphalt. This is because the increase of crumb rubber content in the asphalt increases the possibility of agglomeration between crumb rubber. When the interaction temperature is less than 220°C, the swelling of the crumb rubber in the asphalt is a key factor affecting the performance of the binder. When the interaction temperature is greater than 220°C, the desulfurization and depolymerization of the crumb rubber in the asphalt gradually replaces the swelling and gains the upper hand. When the interaction temperature reaches 260°C, the softening point difference of the modified asphalt is almost close to zero, indicating that the degree of desulfurization and depolymerization of the crumb rubber in the asphalt is already high. It can be seen from **Table 4** that if soluble crumb rubber is used to prepare TB asphalt, in order to avoid serious segregation, the soluble crumb rubber content in the asphalt should not be greater than 15%.

Rotational Viscosity

Viscosity is often used to characterize the friction of molecules inside asphalt during flow. Construction compaction temperature can be determined by viscosity-temperature curves, the larger the viscosity, the higher the compaction temperature (Lo Presti et al., 2014; Xiao et al., 2015). Asphalt aging increases the proportion of asphaltenes, thereby increase the polarity. In general, the increment of polarity decline the fluidity of asphalt, and consequently increase the viscosity (Zhang et al., 2020). So, viscosity is also used to characterize the degree of aging of asphalt. TB asphalt is prepared at high temperature and crumb rubber is decomposes into small molecular substances, which reduces the viscosity of the binder and is beneficial to construction application. Asphalt Rubber Usage Guide stipulates that the 177°C viscosity of TB asphalt should be less than 1.5 KPa

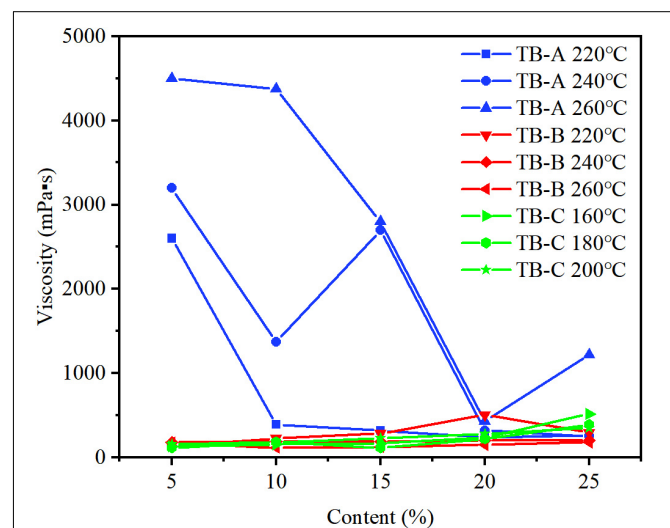
(State of California Department of Transportation, 2003). The 177°C viscosity of TB asphalt prepared by different methods was measured with rotary viscometer.

As shown in **Figure 9**, the 177°C viscosity of TB-B asphalt and TB-C asphalt meets the requirements of the specification. But, the viscosity of TB-A asphalt is much greater than that of TB-B asphalt and TB-C asphalt. This is because the excessive aging of TB-Asphalt increases the asphaltene content. Moreover, 20% is the optimal dosage to control viscosity for TB-A. In addition, the preparation temperature is a key factor affecting the viscosity of TB-B asphalt. As can be seen from **Figure 9**, the higher the temperature, more adequate the desulfurization and depolymerization of crumb rubber, and the lower the viscosity.

FTIR Test Results and Analysis

Samples of TB-A, TB-B prepared with 15% crumb rubber content at 260°C and TB-C prepared with 15% at 180°C were used to carried out FTIR and TG analysis.

Fourier Transform Infrared spectrometer has been widely used in qualitative and quantitative analysis of organic compounds. The modification mechanism and aging degree

**FIGURE 9** | 177°C viscosity of TB asphalt.

of asphalt can be explored by identifying the differences in the absorption spectrum functional groups in the asphalt at the molecular level (Zhang et al., 2020).

Figure 10 is the FTIR spectrum of TB asphalt and base asphalt, the peak at 3437.62 cm^{-1} is attributed to the stretching vibration of the intermolecular hydrogen bond, and the peaks at 2853.18 and 2924.07 cm^{-1} are caused by the $-\text{CH}_2-$ functional group. In the range of ($4000\sim 1300\text{ cm}^{-1}$), the absorption rate of TB asphalt is significantly smaller than base asphalt, indicating that the light component content of TB asphalt are lower compared to base asphalt. The peak at 1600.12 cm^{-1} is generated by the vibration of the $\text{C}=\text{C}$ conjugated double bond in benzene ring. Peaks at 1459.89 and 1376.77 cm^{-1} represent the asymmetric vibration and umbrella vibration of the methyl group (CH_3), respectively. In the fingerprint region ($1300\sim 400\text{ cm}^{-1}$), the peaks at 742.27 and 811.92 cm^{-1} represent the $\text{C}=\text{C}$ of the benzene ring. The peak at 1031.23 cm^{-1} corresponds to the aromatic compounds in asphalt. However, the absorption rate of TB asphalt in this range is also lower than base asphalt, which indicates that the crumb rubber in TB asphalt has absorbed the aromatic compounds of asphalt. The peak at 1103.43 cm^{-1} appearing in both TB-A and TB-B spectrum is due to the contraction vibration of the sulfoxide group ($\text{S}=\text{O}$)., But compared to TB-A, TB-B has a smaller absorption peak area., which means the asphalt aging occurs in the preparation process of both of them, but the aging degree of TB-B is less. Furthermore, the absorption rate of peak at 1600 cm^{-1} in TB-C is slightly lower than TB-A and TB-B, which illustrates that the aging degree of TB-C is less due to its low preparation temperature (Huang et al., 2017).

Thermogravimetric Analysis

Thermogravimetric analyzer is a technique that uses a thermal balance to measure the relationship between the mass of materials and temperature under a program-controlled temperature. It is

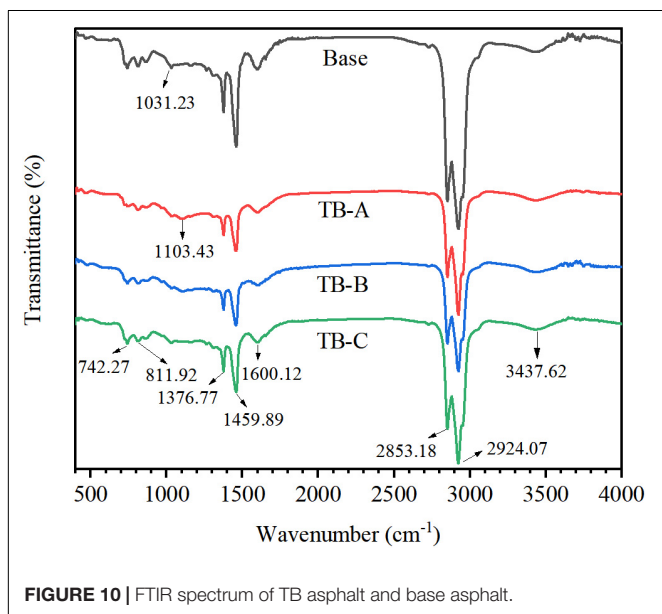


FIGURE 10 | FTIR spectrum of TB asphalt and base asphalt.

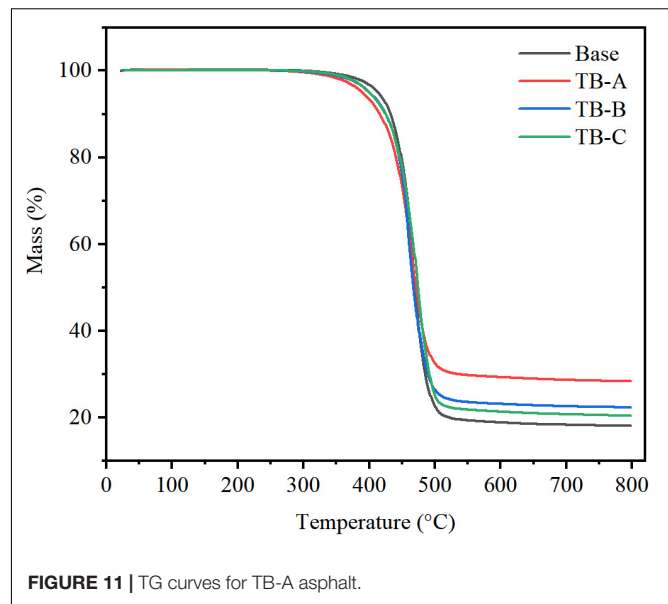


FIGURE 11 | TG curves for TB-A asphalt.

used to study the thermal stability and composition of materials (Chen et al., 2019).

Figure 11 displays the mass change of TB asphalt with temperature. There are three main stages, the first is from room temperature to 250°C , there is almost no mass loss. The second is from 250 to 390°C , and mass-loss in this stage mainly comes from the decomposition of light components such as saturated and aromatic components and small molecular polymers. The third is from 390 to 530°C and the largest mass-loss occurs. That is because a large number of small molecular substances is generated from complex and **vigorously** chemical reaction.

During thermal weightlessness, the higher the aging degree, the larger the mass residual rate (Chen et al., 2019). The reason is that the component easily decomposing converts into relatively stable macromolecular structure, which increases the intermolecular force and thermal stability (Venudharan et al., 2018). From **Figure 11** one can see that the residual rate of TB-A is the highest compared to the base asphalt and is increased by 10.4% compared to base asphalt. Meanwhile, the residual rate of TB-B and TB-C asphalt are only 4.3 and 2.4% higher than those of base asphalt. This once again shows that the aging of the binder during the preparation of TB-A asphalt is more serious.

CONCLUSION

In this study, to avoid excessive aging of TB asphalt during the preparation process, TB-B and TB-C asphalt were prepared using crumb rubber under nitrogen environment and soluble crumb rubber under atmospheric environment. The performance of TB-B and TB-C was compared with TB-A asphalt prepared using crumb rubber in the atmospheric environment. The physical properties, rheological properties, storage stability, and viscosity of the three TB asphalt were tested. Besides, in order to further analyze the aging degree and microscopic modification mechanism of TB-B and TB-C asphalt, the chemical analysis and

thermal analysis of TB asphalt and base asphalt were conducted. The main summary is as follows:

- (1) Chemical analysis and thermal analysis show that the aging degree of TB-B and TB-C asphalt is greatly reduced compared to TB-A, and the aging degree of TB-B is slightly greater than TB-C.
- (2) Through research on the physical and rheological properties of the three TB asphalts, it is found that TB-B asphalt has a lower resistance to deformation at high temperatures than TB-C asphalt, but has the best low temperature performance.
- (3) For the 177°C rotational viscosity of the three TB asphalts, the largest is TB-A and the smallest is TB-B. The viscosity of TB-B and TB-C are less than 1.5 MPa, indicating that the workable performance of TB-B and TB-C meets the requirements.
- (4) Based on comprehensive properties, the optimal preparation process of TB-B is: the content of crumb rubber in asphalt is 15%, the shearing temperature is 260°C, the shearing time is 3 h, and the shearing speed is 4000 r/min. The recommended preparation process of TB-C is: the content of crumb rubber in the asphalt is 15%, the interaction temperature is 180°C, the shearing time is 1h, and the shearing speed is 4000 r/min.
- (5) Using soluble crumb rubber under atmospheric environment and crumb rubber under nitrogen environment are both effective methods to inhibit asphalt aging during preparation process, but both have certain

shortcomings. Such as TB-B asphalt has insufficient resistance to rutting at high temperatures and the storage stability of TB-C is not ideal, and we will conduct in-depth research and propose solutions in our follow-up work.

DATA AVAILABILITY STATEMENT

All datasets presented in this study are included in the article/supplementary material.

AUTHOR CONTRIBUTIONS

JX is the supervisor of this research work and responsible for the editing and writing of manuscript. YZ conducted the experiments and performed the characterization and data analysis. YY helped in samples testing and data analysis. All authors involved the analysis of experimental data and manuscript preparation.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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