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Short-Term Aging Effect on Properties of Sustainable Pavement Asphalts Modified by Waste Rubber and Diatomite

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Abstract: Waste utilization has gained more and more interest. In this study, crumb rubber and diatomite were used to modify asphalt binder and the short-term aging effects on the properties of modified asphalts were evaluated. Three kinds of modified asphalt were prepared; they are diatomite modified asphalt (DA), crumb rubber modified asphalt (RA), and diatomite and crumb rubber compound modified asphalt (DRA). Thin film oven test (TFOT) was used to simulate short-term aging in the laboratory. Penetration, softening points, ductility, viscosity, elastic recovery, low temperature creep, and rutting susceptibility were tested and analyzed before and after TFOT. The results indicated that the softening point, viscosity, elastic recovery, creep stiffness, and $G^*/\sin\delta$ of DA, RA, and DRA are all linearly increased with increasing age, while the penetration and ductility are linearly decreased with increasing age. High temperature properties of asphalt are obviously improved by the addition of crumb rubber. Low temperature properties of asphalt are affected more seriously by the addition of diatomite. DRA could combine the advantages of diatomite and crumb rubber and achieve better performance in short-term aging resistance than DA and RA.

Keywords: modified asphalt; crumb rubber; diatomite; thermal oxidative aging; property analysis

1. Introduction

In recent years, numerous industrial wastes were generated in the world. Reuse of waste materials has received great attention with the aim to reduce the consumption of natural resources and alleviate the accumulation of waste in landfills [1]. Waste tires are regarded as the largest and problematic waste materials due to their large quantity and durability, which may pose a great threat to human health and cause serious environmental risks. Millions of used tires are produced each year because of the increasing number of vehicles in the world. The amount of end-of-life tires (ELTs) is approximately 290 million each year in the US, 355 million in Europe, and 200 million in China [2–4].

Scrap tires can be recycled in the form of crumb rubber (CR), which is a profitable practice. Current research results show that crumb rubber modified asphalt mixture possesses favorable environmental effectiveness. La Rosa et al. [5] demonstrated that the addition of 50 phr of ground tire rubber (GTR) in Styrene–isoprene–styrene (SIS) formulation presents favorable environmental benefits. Life cycle assessment (LCA) results indicate that the effects of virgin rubber (47.1%) and carbon black (34.3%) on the environmental impacts of GTR are more obvious than that of the tire grinding process (4%). Farina et al. [6] investigated the environmental performance of using crumb rubber in bituminous mixtures based on LCA. Results reveal that asphalt rubber obtained through a wet process presents significant benefits for energy saving, environmental impact, human health, preservation of ecosystems, and minimization of resource depletion. The reductions of gross energy requirement and global warming potential range between 36% and 45% compared with standard paving solutions. Moreover, it is an effective method to consume the scrap tires by use of crumb rubber for asphalt modification, which has been widely used in asphalt pavement applications. Crumb rubber modified asphalt and mixture have performed favorably. Addition of crumb rubber can increase the asphalt film thickness, binder resiliency, viscosity, storage stability, rheological property, and shear strength [2,7,8]. Meanwhile, it can improve the mixture performances such as rutting resistance, crack resistance, fatigue resistance, and elastic performance [9–13]. Peralta et al. [12] quantified and correlated the changes in bitumen and rubber during the production of asphalt rubber binders. It indicates that all physical and rheological properties of the asphalt rubber binders are enhanced compared with that of the base bitumen. Manosalvas-Paredes et al. [13] investigated the properties of stone mastic asphalt (SMA) 11 mixture with rubber-end of life tires. The results show that it can fulfill the water sensitivity tests, binder drainage, and resistance to permanent deformation.

Diatomite is siliceous sedimentary rock with a chemical composition of silica, alumina, and iron oxide [14]. Diatomite is a widely used mineral material due to its low cost and considerable storage, the reserves of which are over 300 million tons in China. It possesses high absorptive capacity and stability that has been verified to be effective for asphalt modification [14–18]. Tan et al. [15] demonstrated that the addition of diatomite into asphalt does not generate new functional groups. Cheng et al. [16] found that diatomite can improve the high temperature performance, storage stability, rutting resistance, and long term aging resistance of asphalt. Moreover, high and medium temperature performances of diatomite asphalt mastic are superior to that of limestone, hydrated lime, and fly ash. Guo et al. [17] presented that diatomite can reduce the thermal conductivity and low temperature deformation ability of asphalt mixture. Currently, the study on crumb rubber and diatomite compound modified asphalt is still limited. A more favorable pavement material can be obtained if the compound modified asphalt possesses the advantages of both diatomite and crumb rubber modified asphalt pavement.

The oxidation of asphalt is one of the main factors that causes damage to asphalt pavement. Asphalt aging occurs during the mixing, paving, compacting, and service procedure of asphalt pavement [19]. Asphalt turns into brittle material gradually over time, which is beneficial in terms of rutting resistance. However, it is more prone to crack at low temperature [20]. Some studies have been conducted to investigate the thermal-oxidative aging behavior of rubber modified asphalt and diatomite modified asphalt [20–24]. Cheng et al. [20] studied the effects of diatomite and mineral powder on aging properties of asphalt. The results reveal that diatomite presents better anti-aging effects than mineral powder. Al-Mansob et al. [22] investigated the physical and rheological properties of unmodified and epoxidized natural rubber modified asphalt and the effect of short-term aging and long-term aging on the rheological properties of unmodified and modified asphalts. The results indicate that the aged rubber modified asphalt presents better physical and rheological properties than the base asphalt, which can increase the durability of asphalt pavements. Wang et al. [24] investigated the thermo oxidative aging mechanism of crumb rubber modified asphalts. The results show that the thermo oxidative aging resistance of crumb rubber modified asphalts was improved with increasing crumb rubber dosage. However, the composite influences of diatomite and crumb rubber on thermal oxidative aging properties of asphalt have not been studied.

In this study, crumb rubber and diatomite were used to modify asphalt binder and the short-term aging effects on the properties of modified asphalts were investigated. Diatomite modified asphalt (DA), crumb rubber modified asphalt (RA), and diatomite-crumb rubber compound modified asphalt (DRA) were prepared by wet process in the laboratory. The thin film oven test (TFOT) was used to simulate short-term aging. Tests including penetration, softening point, ductility, viscosity, elastic recovery, low temperature creep, and rutting susceptibility were conducted before and after TFOT. The short-term thermal oxidative aging performances for DA, RA, and DRA were evaluated.

2. Materials and Methods

2.1. Raw Materials

The base asphalt AH-90 used for the experiments was from Panjin Petrochemical Industry, Liaoning Province of China. Physical properties of AH-90 asphalt were measured and are listed in Table 1. Crumb rubber particle was obtained from Changchun Yuxing Rubber Materials Co., Ltd., Changchun, Jilin Province, China. Physical properties and corresponding particle distribution of crumb rubber are given in Tables 2 and 3. Diatomite was produced by Changchun Diatomite Products Co., Ltd., Changchun, Jilin Province, China. Physical properties and particle distributions for diatomite are listed in Tables 4 and 5.

Table 1. Properties of neat asphalt. TFOT stands for thin film oven test.

Property	Value	Technical Criterion (%)
Penetration (25 °C, 0.1 mm)	84	80~100
Penetration index, PI	−1.01	−1.5~+1.0
Softening point (The Ring and Ball Test, TR&B) (°C)	44	≥42
Ductility (15 °C, cm)	150	≥100
Specific gravity (15 °C, g/cm^3)	1.05	-
After TFOT		
Mass loss (%)	−0.3	≤±0.8
Penetration ratio (25 °C, %)	64	≥57
Age ductility (10 °C, cm)	14	≥8

Table 2. Properties of crumb rubber.

Property	Sauer A Hardness (°)	Apparent Density (g/cm^3)	Moisture Content (%)
Value	60	1.321	0.5

Table 3. Particle distribution of crumb rubber.

Particle Size (μm)	550	380	270	250	212	180	160	150	120
Percentage passing (%)	69.8	33.5	20.8	13.8	5.3	5.1	3.9	3.0	0.0

Table 4. Properties of diatomite.

Property	Color	PH	Specific Gravity (g/cm^3)	Bulk Density (g/cm^3)	Loss on Ignition (%)	Content of SiO_2 (%)	Content of Fe_3O_2 (%)
Value	Orange	8~10	2.152	0.37	≤0.25	≥87.1	≤1.1

Table 5. Particle distribution of diatomite.

Particle Size (μm)	<5	10~5	20~10	40~20	>40
Percentage (%)	19.3	28.0	20.7	21.0	11.0

2.2. Preparation of Modified Asphalt Binder

In this study, three kinds of modified asphalt were prepared: diatomite modified asphalt (DA), crumb rubber modified asphalt (RA), and diatomite and crumb rubber compound modified asphalt (DRA). Wet process was widely adopted to prepare the modified asphalt binders [11,25–27], which can make crumb rubber, diatomite, and asphalt react for a period and take advantage of the benefits of all base ingredients [4]. A high speed shear homogenizer [20] was employed to stir the modified asphalt (shown in Figure 1), the oil bath as a heating device can control the temperature of the modified asphalt when stirring. The preparation process mainly included three steps: heating of raw materials; shearing and mixing of ingredients; and storing of modified asphalt binder. Corresponding optimal or suggested preparation parameters of DA, RA, and DRA have been determined in previous research [16,28,29]. The detailed preparation processes were as follows:

In the preparation of DA, the content of diatomite 12.8% (by the weight of asphalt) was adopted. The specific preparation steps were as follows: (1) Diatomite and asphalt were separately placed in the oven at 140 °C for 4 h to make sure that the asphalt flowed sufficiently and diatomite reached the blending temperature. (2) Diatomite and asphalt were mixed using the high-shear homogenizer with a speed of 4000 rpm, and the blending was conducted for 40 min at 150 °C in order to ensure that diatomite distributed uniformly in asphalt [16].

In the preparation of RA, the content of crumb rubber 18% (by the weight of asphalt) was used. Specifically, (1) neat asphalt and crumb rubber were separately heated in the oven at 140 °C for 4 h, thus, asphalt was at a fluid state that can be easily stirred. (2) The crumb rubber was added into the asphalt, which was placed into the shear homogenizer after preliminary mixing. (3) Shear temperature and speed were set to 180 °C and 5000 rpm, respectively. The blend of asphalt and crumb rubber was mixed and sheared for 45 min after the temperature of the blend reached 180 °C. (4) The blended mix was contained in the shear homogenizer and allowed to swell for 60 min [28].

In the preparation of DRA, the contents of diatomite and crumb rubber were 6.2% and 13.8% (by the weight of asphalt), respectively. The preparation steps of DRA were the same as those of the RA except the shear temperature, shear speed, shear time, and swelling time were 183 °C, 5300 rpm, 55 min, and 49 min, respectively [29].

Figure 1. High speed shear homogenizer.

2.3. Characterization Method

Thin film oven test (TFOT) and rolling thin film oven test (RTFOT) are the most widely used methods for short term oxidative aging simulation of asphalt [30–32]. Current research results indicate that the results from TFOT and RTFOT present strong correlation. The methods present similar severities for measurements with different parameters [30]. In this study, TFOT was used for short term oxidative aging simulation in accordance with ASTM D 1754. Asphalt amount was 50 g in an iron pan, which was placed on the tray. The axis of revolution was vertical. In order to analyze the short term aging systematically and make the aging law of asphalt clear during the early age, the aging was conducted at 163 °C for 0, 1, 2, 3, 4, and 5 h.

Penetration is a useful property to evaluate the consistency of asphalt at intermediate service temperatures [33]. It is the depth in units of 1/10 mm that a standard needle with a load of 100 g penetrates into the asphalt vertically in a time period of 5 s. In this study, penetration of modified asphalt was tested using penetration test instrument (DF-4, Beijing Zhonghangkegong Instrument Co., Ltd., Beijing, China) at 25 °C according to ASTM D5 before and after TFOT. Percent retained penetration (PRP) was calculated and used to evaluate the anti-aging effects on properties of DA, RA, and DRA, which can be obtained by

$$PRP = \frac{P_2}{P_1} \tag{1}$$

where P_1 and P_2 are the penetrations before and after TFOT, respectively.

Softening point is a widely used parameter to evaluate high temperature susceptibility of asphalt. It is the temperature at which a phase change occurs [20]. The Ring and Ball Softening Point test (TR&B) (SYD-2806, Beijing Zhonghangkegong Instrument Co., Ltd., Beijing, China) was used to measure the temperature at which the asphalt could not support the steel ball with the weight 3.5 g at the heating rate 5 °C/min according to ASTM D36. Increment of softening point (ΔT) can be calculated and used to evaluate the aging degree [14], which can be obtained by

$$\Delta T = T_2 - T_1 \tag{2}$$

where T_1 and T_2 are the softening points before and after TFOT, respectively.

Ductility is a method to indirectly evaluate the tensile cohesive property of asphalt. It is the distance in centimeters to which the sample can be elongated before breaking when two ends of a sample are pulled apart at a specified temperature and speed [22]. In this study, ductility of modified asphalt was tested using a ductility test instrument (LYY-7, Beijing Zhonghangkegong Instrument Co., Ltd., Beijing, China) at 15 °C and a speed of 5 cm/min according to ASTM D113.

Viscosity reflects the flow characteristics of asphalt, which directly affects the workability of the asphalt mixture [14,22]. A Brookfield viscometer (SD-0625, Shanghai Geology Instrument Institute, China) was used to measure the rotational viscosity of crumb rubber and diatomite compound modified asphalt at 135 °C according to ASTM D4402. Viscosity aging index (*VAI*) was applied to investigate the effect of aging on the shearing resistance of asphalt. A higher *VAI* indicates a more serious aging pattern [14]. *VAI* can be calculated by the following equation.

$$VAI = \lg[\lg(\eta_2 \times 1000)] - \lg[\lg(\eta_1 \times 1000)] \tag{3}$$

where η_1 and η_2 are the viscosities before and after TFOT, respectively.

Elastic recovery reflects the deformation recovery property of asphalt after being elongated. A degree of elastic recovery is desirable in pavement to avoid permanent deformation. The elastic recovery of asphalt is tested by use of a ductility test instrument (LYY-7, Beijing Zhonghangkegong Instrument Co., Ltd., Beijing, China), which is used to elongate an asphalt specimen at a constant rate. After a period of time, the elongated specimen is cut and then allowed to rest. After the period of rest is complete, the distance between the ends of the cut specimen is measured. The elastic recovery is the ratio of the difference in elongation between cutting and the end of the rest period to the total elongation [28].

$$ER = \frac{E_b - E_a}{E_b} \times 100 \tag{4}$$

where ER is elastic recovery of asphalt, %; E_b is the elongation of asphalt specimen before cutting; and E_a is the elongation after the period of rest.

The bending beam rheometer (BBR) test was used to investigate the low temperature creep property of modified asphalt. The size of beam sample was 125 mm × 12.5 mm × 6.25 mm, which was submerged in an ethyl alcohol bath at −12 °C for 60 min before tests. Creep tests were carried out at −18 °C by a bending beam rheometer (TE-BBR, Cannon Instrument Company, Harrisburg, PA, USA). Deflection at the mid-span point of the beam was measured continuously under constant loads, and creep stiffness (S) was determined according to ASTM D 6648.

The dynamic shear rheometer (DSR) test was used to investigate the rheological properties of modified asphalt at high and intermediate temperatures. Rheological parameters, including complex modulus ($G*$) and phase angle (δ), can be measured. The DSR test (DSR, Malvern Instruments Ltd., Malvern, UK) was conducted at 70 °C. The rutting parameter ($G*/\sin\delta$) was used to evaluate the rutting susceptibility of asphalts, which can be determined by the measured $G*$ and δ according to ASTM D 5801.

3. Results and Discussion

3.1. Penetration

The penetrations of asphalt mastics after 1 h, 2 h, 3 h, 4 h, and 5 h aging were tested at 25 °C before and after TFOT in order to investigate the consistency of DA, RA, and DRA. Results are shown in Figure 2.

It can be seen from Figure 2 that penetrations of DA, RA, and DRA linearly decrease with increasing time. The R^2 are higher than 0.97, which means that the linear fittings are favorable. However, the speed of descent varies for the three mastics. Penetration slopes of DA, RA, and DRA are −5.5106, −3.2049, and −1.5503, respectively. The lower the slope is, the faster the penetration decreases. This indicates that the effect of oxidation aging on penetration of DA is the most significant, followed by RA, and DRA.

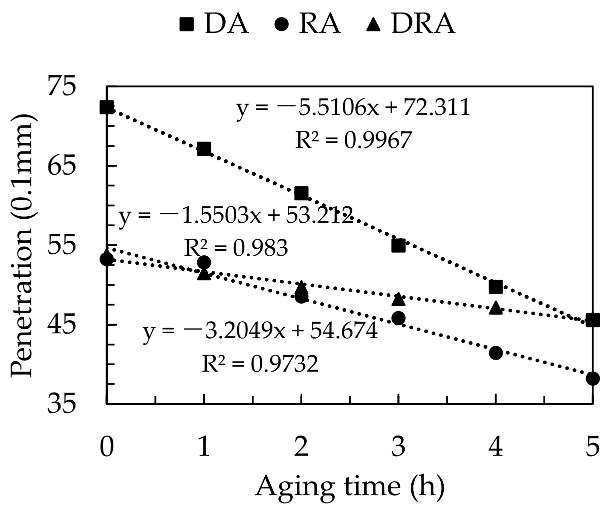

Figure 2. The penetration versus aging time of diatomite modified asphalt (DA), crumb rubber modified asphalt (RA), and diatomite and crumb rubber compound modified asphalt (DRA).

In order to quantitatively analyze the anti-aging properties of the three mastics, the PRP of the three mastics was calculated according to Equation (1), and the results are listed in Table 6. As shown in Table 6, the PRP of DA, RA, and DRA are 72.79%, 75.71%, and 84.54%, respectively. Yu et al. [33] indicated that the higher PRP is, the less aging has occured. Therefore, it can be concluded that DRA has better anti-aging properties than DA and RA. The reasons is that diatomite particles can effectively adsorb the small molecular groups and low polar aromatic molecules of asphalt, which inhibits the aging reaction significantly [27]. The crumb rubber would be degraded in the high temperature blending process, and the degradation product distributed as resins and asphaltenes in asphalt [21]. The compound modified asphalt could combine the advantages of diatomite and crumb rubber, and achieve better modification effects.

Table 6. Percent retained penetration (PRP) of DA, RA, and DRA.

Type	P_1 (0.1 mm)	P_2 (0.1 mm)	PRP (%)
DA	72.36	45.54	62.93
RA	53.23	38.17	71.71
DRA	53.75	45.78	85.17

3.2. Softening Point

The softening points of asphalt mastics were tested before and after TFOT in order to estimate the effect of aging on high temperature stability, and the results are shown in Figure 3.

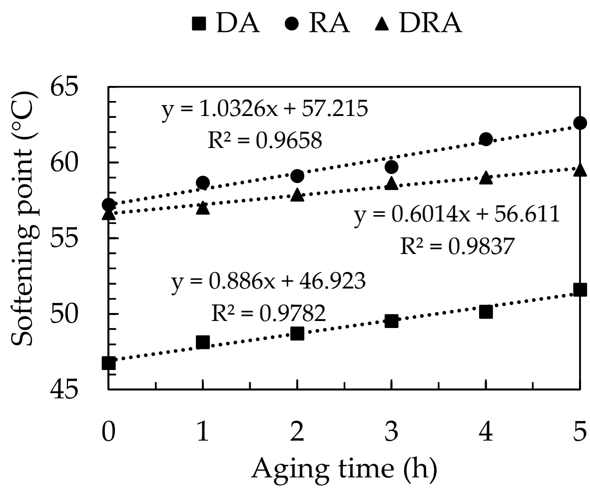

Figure 3. The softening point versus aging time of DA, RA, and DRA.

As shown in Figure 3, the softening points of DA, RA, and DRA linearly increase with increasing time. Volatilization of small molecule components in asphalt and chemical reaction between aromatics and oxygen are the main reasons leading to the aging of asphalt. Generally, in the asphalt aging process, saturations are relatively stable and change little; aromatics are more prone to turn into resins with oxidative polymerization reaction; resins containing polar functional groups are prone to turn into asphaltenes with aggregation and condensation reaction [21]. The asphalt components generally transform into the heavy direction of aromatics–resins–asphaltenes. Therefore, softening points of DA, RA, and DRA are increased after aging. It can be found that the softening point of RA is the highest among the three mastics, and the increasing speed of RA is the fastest because the slope of fitting line of RA is the biggest. It means that the effect of aging on the softening point of RA is the most significant. It is probably because the swelling process of rubber is still acting during the aging process, which accelerates the transformation of small molecule components to resin and asphaltenes. This results in the most serious aging of RA according to results of the softening point.

Table 7 lists the increments of softening point of DA, RA, and DRA. It can be seen that the ΔT of RA is the biggest, followed by DA and DRA. This indicates that the effect of oxidation aging on RA is the most significant, while it is the lowest on DRA. Therefore, the anti-aging property of composite modified asphalt is excellent.

Table 7. ΔT of DA, RA, and DRA.

Type	T_1 (°C)	T_2 (°C)	ΔT (°C)
DA	46.75	51.59	4.84
RA	57.21	62.61	5.40
DRA	56.65	59.51	2.86

3.3. Ductility

The ductility tests were carried out at 15 °C before and after TFOT in order to evaluate the anti-aging effect of DA, RA, and DRA on tensile cohesive properties. Results of ductility tests are shown in Figure 4.

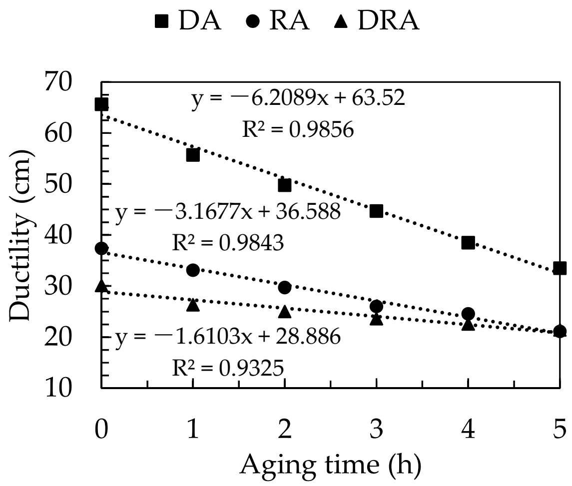

Figure 4. The ductility versus aging time of DA, RA, and DRA.

As presented in Figure 4, ductility of DA, RA, and DRA linearly decrease with increasing time. This is mainly because that aromatics are volatilized or transformed into asphaltenes and resins. Asphalts become harder. The regressive coefficients R^2 are higher than 0.93, which means that the linear fittings are successful. Regressive slopes of DA, RA, and DRA are −6.2089, −3.1677, and −1.613, respectively. The lower the slope is, the faster is the ductility decrease. This indicates that the effect of thermal oxidation aging on the ductility of DA is the most significant, followed by RA and DRA. However, the RA is considered to be the most affected mastic among the three mastics according to the results of softening point. These two conclusions are inconsistent. It is because the crumb rubber is a polymer and presents with better ductility and plasticity when compared with diatomite. The result is that the aggressive slope of DA is the lowest among the three mastics. The compound modified asphalt combines the advantages of diatomite and crumb rubber and obtains better modification effects.

3.4. Viscosity

In order to investigate the effect of aging on the viscosity of DA, RA, and DRA, rotational viscosities of the asphalt mastics were tested before and after TFOT at 135 °C. The results of viscosity tests are shown in Figure 5.

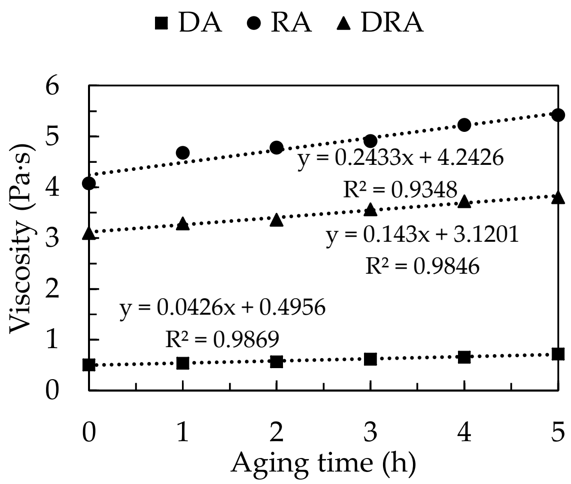

Figure 5. The viscosity versus aging time of DA, RA, and DRA.

As shown in Figure 5, the viscosity of DA, RA, and DRA all increased with increasing time. They exhibit a significant linear relationship between viscosity and aging time. Viscosity represents the shearing deformation resistance that affects the construction of asphalt pavement. The higher the viscosity, the better is the property of deformation resistance. However, it would be too hard to blend and compact if the viscosity is too high. Therefore, the viscosity should be controlled in a reasonable duration. The regressive coefficients R^2 are all higher than 0.93, which means that the linear fittings are successful. Regressive slopes of DA, RA, and DRA are 0.0426, 0.2433, and 0.143, respectively. The higher the slope is, the faster is the viscosity increase. This indicates that the effect of thermal oxidation aging on viscosity of RA is the most significant, followed by DRA, and DA.

Viscosity aging index (*VAI*) is a common index which is used to evaluate the aging degree of asphalt after TFOT. Table 8 lists the *VAI* of DA, RA, and DRA. It can be seen that the *VAI* of DA is the highest, followed by RA and DRA. This indicates that the effect of oxidation aging on viscosity of DA is the most significant. The results are not consistent with the regressive slope. This is because of the different calculation strategy for regressive slope and *VAI*. The slope is a ratio of viscosity to aging time and *VAI* is the difference of viscosity before and after TFOT. Besides, the viscosity of DA is too small in comparison with the viscosities of RA and DRA. The differences of viscosities between DA and DRA are nearly an order of magnitude, which results in the different results of regressive slope and *VAI*. Considering the calculative principle of the two methods, the results of *VAI* are more reasonable. Therefore, the anti-aging on viscosity of DRA is considered to be the best.

Table 8. Viscosity aging index (*VAI*) of DA, RA, and DRA.

Type	η_1 (Pa·s)	η_2 (Pa·s)	*VAI*
DA	0.504	0.721	0.0242
RA	4.078	5.423	0.0146
DRA	3.106	3.805	0.0108

Furthermore, the viscosity-temperature relationships of DA, RA, and DRA were analyzed via the equiviscosity principle. The curves of viscosity-temperature before and after TFOT are illustrated in Figure 6.

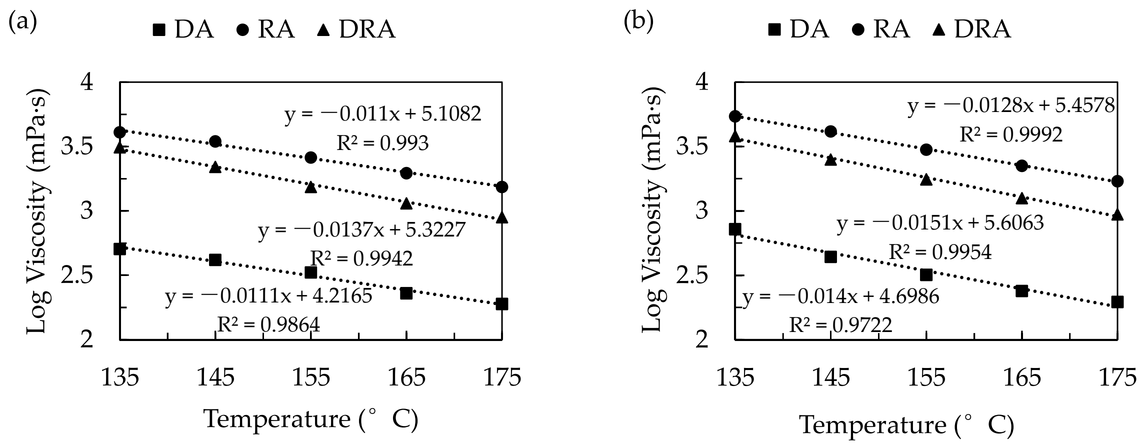

Figure 6. The viscosity versus temperature of DA, RA, and DRA (**a**) before TFOT and (**b**) after TFOT.

It can be seen from Figure 6 that the Log viscosities of DA, RA, and DRA linearly decrease with increasing temperature. The regressive coefficients R^2 are higher than 0.97, which means that the regression analyses are reliable. The regressive absolute slopes of DRA both before and after aging are highest among the three mastics, which suggests that DRA would have a relatively lower viscosity at high temperature and have a greater viscosity at low temperature. This is beneficial for its application in the construction of asphalt pavement. The ranges of mixing and compaction temperature could be calculated by the viscosity-temperature relationship corresponding to viscosity range 0.15~0.19 Pa·s and 0.25~0.31 Pa·s according to the Chinese standard specification (JTG E20-2011) [34]. Results are listed in Table 9.

Table 9. Mixing and compaction temperature of DA, RA, and DRA.

Type	Mixing Temperature (°C)		Compaction Temperature (°C)	
	Unaged	Aged	Unaged	Aged
DA	174.6~183.8	172.8~180.2	155.4~163.8	157.6~164.3
RA	257.2~266.5	248.4~256.4	237.9~246.4	231.7~239.0
DRA	222.2~229.7	220.4~227.2	206.6~213.5	206.3~212.5

It can be seen that the mixing and compaction temperature of RA is highest, followed by DRA and DA. The absolute differences of mixing temperature range between before and after aging are 1.8~3.6 °C, 8.8~10.1 °C, and 1.8~2.5 °C for DA, RA, and DRA, respectively. The absolute differences of compaction temperature range between before and after aging are 2.2~0.5 °C, 6.2~7.4 °C, and 0.3~1 °C for DA, RA, and DRA, respectively. Effect of aging on mixing and compaction temperature of DRA is the slightest. The conclusion is consistent with the result of *VAI*. Thus, the anti-aging of DRA is considered to be the best according to the viscosity test.

3.5. Elastic Recovery

Elastic recoveries of modified asphalts were tested at 20 °C and the results are shown in Figure 7. As shown in Figure 7, elastic recovery of DA, RA, and DRA are all linearly increased with increasing time. It is possible that the aromatics in asphalt decrease after aging, in contrast, elastic components of asphalt increase, which improves the elastic recovery property of DA, RA, and DRA. However, the increments of RA and DRA are more obvious than that of DA. This is mainly because the swelling process of rubber is still acting during the aging process and more dissolved crumb rubber dissolves in asphalt, which promotes the improvement of elastic recovery ability of RA and DRA [35]. The elastic recoveries of RA and DRA are significantly higher than that of DA. This is because diatomite is a mineral while crumb rubber is a polymer. There is no chemical reaction during blending of diatomite and asphalt and, therefore, the elastic recovery property could not be improved. On the contrary, the elastic recovery property is distinct for the crumb rubber modifying process because of the swelling reaction and degradation action. They result in the obvious difference of elastic recovery between DA and RA or DRA. A higher elastic recovery of the asphalt binder is favorable as it resists fatigue cracking as well as rutting. Hence, it is expected that RA and DRA would perform better than DA in the low temperature condition.

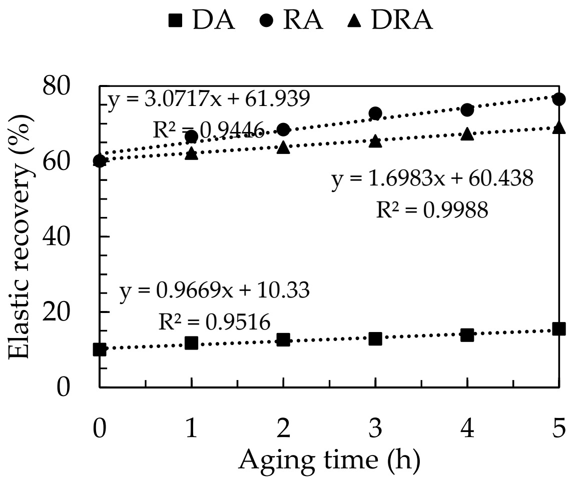

Figure 7. The elastic recovery versus aging time of DA, RA, and DRA

3.6. Low Temperature Creep

Low temperature creep behavior of DA, RA, and DRA was employed to evaluate the effect of aging time on the low temperature property using a bending beam rheometer (BBR). The test temperature was −12 °C. Creep stiffness (*S*) at the time of 60 s were obtained and are shown in Figure 8.

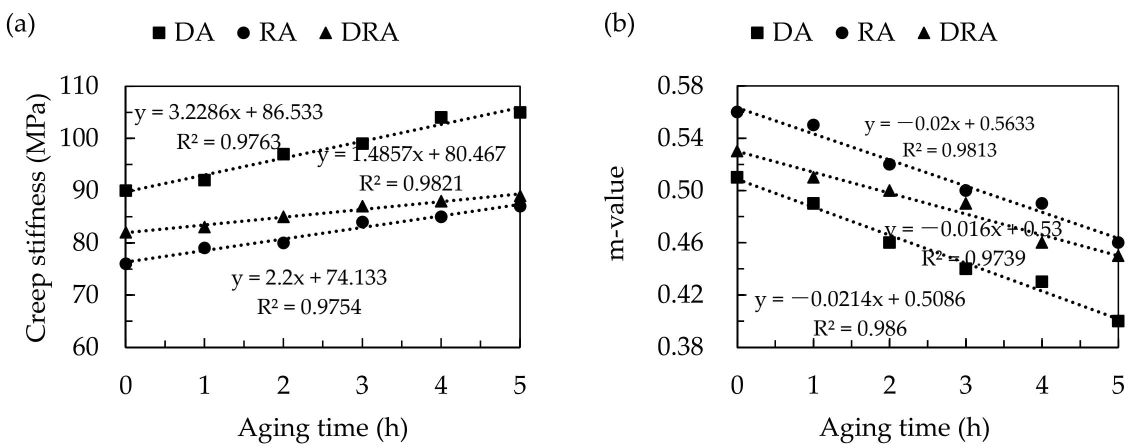

Figure 8. The creep stiffness and *m*-value versus aging time of DA, RA, and DRA; (**a**) creep stiffness, (**b**) *m*-value.

The results shown in Figure 8 reveal that creep stiffness (*S*) of asphalt binders linearly increases while the *m*-value linearly decreases with increasing time. This is because the light component in asphalt transforms into a heavy component, which make the asphalt become harder [20,21]. Thus, the creep stiffness (*S*) increases with increasing time. Creep stiffness (*S*) and *m*-value indicate the susceptibility to low temperature cracking as designated by Strategic Highway Research Program (SHRP). The higher *m*-value and lower creep stiffness of asphalt binders implies better resistance to low temperature cracking. Therefore, the DA is more susceptible to low temperature cracking in comparison with RA and DRA. Regressive slopes of DA, RA, and DRA for creep stiffness are 3.2286, 2.2 and 1.4857, respectively, while they are −0.0214, −0.02 and −0.016 for m-values, respectively. The higher the slope is, the faster is the creep stiffness increase and the slower is the *m*-value decrease [36]. This indicates that the effect of thermal oxidation aging on creep stiffness (*S*) and *m*-value of DA is the most significant, followed by RA and DRA.

3.7. Rutting Susceptibility

Dynamic rheological properties of DA, RA, and DRA before and after aging were measured using a Dynamic Shear Rheometer (DSR) at the temperature of 70 °C, with 25 mm diameter and 1 mm gap size. The complex modulus (G^*) and phase angle (δ) were measured for these tests. The results of rutting parameters ($G^*/\sin\delta$) were calculated and are shown in Figure 9.

As shown in Figure 9, $G^*/\sin\delta$ of DA, RA, and DRA are all increased with increasing time. In addition, the relationships between $G^*/\sin\delta$ and aging time are significantly linear. The higher the $G^*/\sin\delta$ is, the better is the property of rutting deformation resistance. Therefore, it seems that the property of deformation resistance is improved after aging. This could be ascribed to the fact that the asphalt becomes harder after aging. It is consistent with the results of creep stiffness. The susceptibility to low temperature cracking is improved as the asphalt becomes harder. It would be more likely to be cracked at the low temperature.

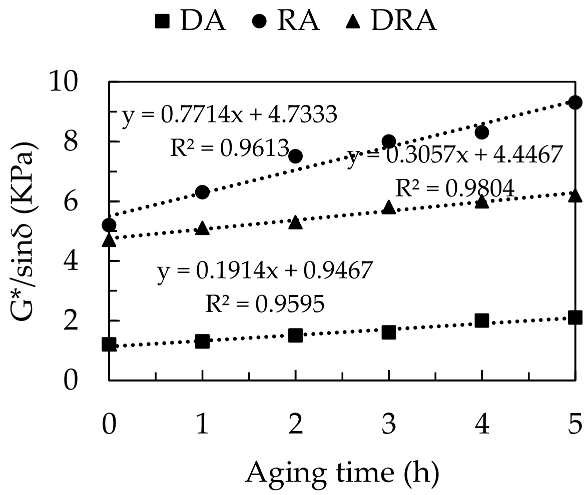

Figure 9. The rutting parameters versus aging time of DA, RA, and DRA.

4. Conclusions

In this paper, short-term aging effects on the properties of DA, RA, and DRA were demonstrated. TFOT was used to simulate short-term aging. Tests including penetration, softening point, ductility, viscosity, elastic recovery, low temperature creep, and rutting susceptibility were conducted before and after TFOT. The short-term thermal oxidative aging performances for DA, RA, and DRA were evaluated and the following main conclusions were obtained:

- The softening point, viscosity, elastic recovery, creep stiffness, and $G^*/\sin\delta$ of DA, RA, and DRA all linearly increased with increasing time, while the penetration and ductility linearly decreased with increasing time. This could be ascribed to the fact that the aging time is not long enough to make the properties of asphalt become stable.

- The anti-aging performance of three types of modified asphalt was evaluated by PRP, ΔT, and *VAI*. According to the results of PRP, DRA exhibits the highest PRP compared with DA and RA, which indicates that DRA has a better performance of aging resistance than DA and RA. Meanwhile, the lower ΔT and *VAI* of DRA illustrates that the anti-aging of DRA is considered to be best.
- High temperature properties of asphalt under short-term aging are affected more seriously by the addition of crumb rubber according to the results of penetration, softening point, viscosity, elastic recovery, and $G^*/\sin\delta$. Low temperature properties of asphalt are affected more seriously by the addition of diatomite according to the results of creep stiffness and m-value. The diatomite and crumb rubber modified asphalt could combine the advantages of diatomite and crumb rubber and achieve better modification effects.

In summary, using diatomite and crumb rubber improves the short-term anti-aging property of asphalt. This can increase the thermal stability of asphalt pavement. Furthermore, tests on the long-term aging effects on properties of compound modified asphalt should be conducted in the future.

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References

1. Amin, M.N.; Khan, M.I.; Saleem, M.U. Performance evaluation of asphalt modified with municipal wastes for sustainable pavement construction. *Sustainability* **2016**, *8*, 949. [CrossRef]
2. Presti, D.L. Recycled tyre rubber modified bitumens for road asphalt mixtures: A literature review. *Constr. Build. Mater.* **2013**, *49*, 863–881. [CrossRef]
3. Shu, X.; Huang, B. Recycling of waste tire rubber in asphalt and Portland cement concrete: An overview. *Constr. Build. Mater.* **2014**, *67*, 217–224. [CrossRef]
4. Liu, H.; Chen, Z.; Wang, W.; Wang, H.; Hao, P. Investigation of the rheological modification mechanism of crumb rubber modified asphalt (CRMA) containing TOR additive. *Constr. Build. Mater.* **2014**, *6*, 225–233. [CrossRef]
5. La Rosa, A.D.; Recca, G.; Carbone, D.; Battiato, S.; Latteri, A.; Cozzo, G.; Cicala, G. Environmental benefits of using ground tyre rubber in new pneumatic formulations: A life cycle assessment approach. *Proc. Inst. Mech. Eng. Part L* **2015**, *229*, 309–317.
6. Farina, A.; Zanetti, M.C.; Santagata, E.; Blengini, G.A. Life cycle assessment applied to bituminous mixtures containing recycled materials: Crumb rubber and reclaimed asphalt pavement. *Resour. Conserv. Recycl.* **2017**, *117*, 204–212. [CrossRef]
7. Wang, Q.; Li, S.; Wu, X.; Wang, S.; Ouyang, C. Weather aging resistance of different rubber modified asphalts. *Constr. Build. Mater.* **2016**, *106*, 443–448. [CrossRef]
8. Liang, M.; Xin, X.; Fan, W.; Sun, H.; Yao, Y.; Xing, B. Viscous properties, storage stability and their relationships with microstructure of tire scrap rubber modified asphalt. *Constr. Build. Mater.* **2015**, *74*, 124–131. [CrossRef]
9. Moreno, F.; Sol, M.; Martín, J.; Pérez, M.; Rubio, M.C. The effect of crumb rubber modifier on the resistance of asphalt mixes to plastic deformation. *Mater. Des.* **2013**, *47*, 274–280. [CrossRef]
10. Palit, S.K.; Reddy, K.S.; Pandey, B.B. Laboratory evaluation of crumb rubber modified asphalt mixes. *J. Mater. Civ. Eng.* **2004**, *16*, 45–53. [CrossRef]

11. Ge, D.; Yan, K.; You, Z.; Xu, H. Modification mechanism of asphalt binder with waste tire rubber and recycled polyethylene. *Constr. Build. Mater.* **2016**, *126*, 66–76. [CrossRef]
12. Peralta, J.; Silva, H.M.; Hilliou, L.; Machado, A.V.; Pais, J.; Williams, R.C. Mutual changes in bitumen and rubber related to the production of asphalt rubber binders. *Constr. Build. Mater.* **2012**, *36*, 557–565. [CrossRef]
13. Manosalvas-Paredes, M.; Gallego, J.; Saiz, L.; Bermejo, J.M. Rubber modified binders as an alternative to cellulose fiber—SBS polymers in Stone Matrix Asphalt. *Constr. Build. Mater.* **2016**, *121*, 727–732. [CrossRef]
14. Cong, P.; Chen, S.; Chen, H. Effects of diatomite on the properties of asphalt binder. *Constr. Build. Mater.* **2012**, *30*, 495–499. [CrossRef]
15. Tan, Y.; Lei, Z.; Zhou, X. Investigation of low-temperature properties of diatomite-modified asphalt mixtures. *Constr. Build. Mater.* **2012**, *36*, 787–795.
16. Cheng, Y.; Tao, J.; Jiao, Y.; Tan, G.; Guo, Q.; Wang, S.; Ni, P. Influence of the properties of filler on high and medium temperature performances of asphalt mastic. *Constr. Build. Mater.* **2016**, *118*, 268–275. [CrossRef]
17. Guo, Q.; Li, L.; Cheng, Y.; Jiao, Y.; Xu, C. Laboratory evaluation on performance of diatomite and glass fiber compound modified asphalt mixture. *Mater. Des.* **2015**, *66*, 51–59. [CrossRef]
18. Cong, P.; Liu, N.; Tian, Y.; Zhang, Y. Effects of long-term aging on the properties of asphalt binder containing diatoms. *Constr. Build. Mater.* **2016**, *123*, 534–540. [CrossRef]
19. Cong, P.; Chen, S.; Yu, J.; Wu, S. Effects of aging on the properties of modified asphalt binder with flame retardants. *Constr. Build. Mater.* **2010**, *24*, 2554–2558. [CrossRef]
20. Cheng, Y.; Tao, J.; Jiao, Y.; Guo, Q.; Li, C. Influence of diatomite and mineral powder on thermal oxidative ageing properties of asphalt. *Adv. Mater. Sci. Eng.* **2015**, *2015*, 947834. [CrossRef]
21. Xiang, L.; Cheng, J.; Kang, S. Thermal oxidative aging mechanism of crumb rubber/SBS composite modified asphalt. *Constr. Build. Mater.* **2015**, *75*, 169–175. [CrossRef]
22. Al-Mansob, R.A.; Ismail, A.; Yusoff, N.I.M.; Albrka, S.I.; Azhari, C.H.; Karim, M.R. Rheological characteristics of unaged and aged epoxidised natural rubber modified asphalt. *Constr. Build. Mater.* **2016**, *102*, 190–199. [CrossRef]
23. Xu, O.; Xiao, F.; Amirkhanian, S.N.; Liu, Y.; Han, S. Long-term aging effect on rheological properties of combined binders from various polymers with ground tire rubber. *Can. J. Civ. Eng.* **2016**, *43*, 451–460. [CrossRef]
24. Wang, S.; Wang, Q.; Li, S. Thermooxidative aging mechanism of crumb-rubber-modified asphalt. *J. Appl. Polym. Sci.* **2016**, *133*. [CrossRef]
25. Wang, H.; You, Z.; Goh, S.W.; Hao, P.; Huang, X. Laboratory evaluation on the high temperature rheological properties of rubber asphalt: A preliminary study. *Can. J. Civ. Eng.* **2012**, *39*, 1125–1135. [CrossRef]
26. Zanzotto, L.; Kennepohl, G. Development of rubber and asphalt binders by depolymerization and devulcanization of scrap tires in asphalt. *Transp. Res. Rec.* **1996**, *1530*, 51–58. [CrossRef]
27. Song, Y.; Che, J.; Zhang, Y. The interacting rule of diatomite and asphalt groups. *Pet. Sci. Technol.* **2011**, *29*, 254–259. [CrossRef]
28. Zhao, S.Y. Research on Pavement Performance and Warm Mix Effect of Rubber Modified Asphalt Mixture. Master's Thesis, Jilin University, Changchun, China, 2014.
29. Pei, M.Z. Research on the Optimized Preparation Process and Anti-Aging Property of Diatomite-Crumb Rubber Compound Modified Asphalt. Master's Thesis, Jilin University, Changchun, China, 2016.
30. Lu, X.; Isacsson, U. Effect of ageing on bitumen chemistry and rheology. *Constr. Build. Mater.* **2002**, *16*, 15–22. [CrossRef]
31. Dehouche, N.; Kaci, M.; Mokhtar, K.A. Influence of thermo-oxidative aging on chemical composition and physical properties of polymer modified bitumens. *Constr. Build. Mater.* **2012**, *26*, 350–356. [CrossRef]
32. Cong, P.; Wang, J.; Li, K.; Chen, S. Physical and rheological properties of asphalt binders containing various antiaging agents. *Fuel* **2012**, *97*, 678–684. [CrossRef]
33. Yu, J.Y.; Feng, P.C.; Zhang, H.L.; Wu, S.P. Effect of organo-montmorillonite on aging properties of asphalt. *Constr. Build. Mater.* **2009**, *23*, 2636–2640. [CrossRef]
34. JTG E20-2011. *Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering*; Research Institute of Highway Ministry of Transport: Beijing, China, 2011. (In Chinese)

35. Zhang, J.; Faruk, A.N.M.; Karki, P.; Holleran, I.; Hu, X.; Walubita, L.F. Relating asphalt binder elastic recovery properties to HMA cracking and fracture properties. *Constr. Build. Mater.* **2016**, *121*, 236–245. [CrossRef]
36. Zhang, H.; Su, M.; Zhao, S.; Zhang, Y.; Zhang, Z. High and low temperature properties of nano-particles/polymer modified asphalt. *Constr. Build. Mater.* **2016**, *114*, 323–332. [CrossRef]