Laboratory Investigation on the Short-term Aging Behavior of Various Highly Modified Asphalt Binders

First author: Quan Lv, Postdoctoral fellow.

The Key Laboratory of Road and Traffic Engineering, Tongji University, Shanghai 201804, China

Email: 1991lvquan@tongji.edu.cn

Second author: Jie Gao, Senior Engineer.

Beijing General Municipal Engineering Design & Research Institute Co., Ltd, Beijing 100082, China

Email: 1254340827@qq.com

Third author: Shaopeng Liu, Senior Engineer.

Transport Planning and Research Institute, Ministry of Transport, Beijing 100028, China

Email: 993696531@qq.com

Fourth author: Chuanqi Yan, Associate Professor.

School of Civil Engineering, Southwest Jiaotong University, Chengdu, Sichuan 610031, China

Highway Engineering Key Laboratory of Sichuan Province, Chengdu, Sichuan, 610031, China

Email: ycq@swjtu.edu.cn

Fifth author: Haixiao Hu, Senior Engineer.

Shandong Provincial Communications Planning And Design Group Co., Ltd, Shandong 250101, China

Email: 384745994@qq.com

Corresponding author and sixths author and: Liyuan Liu, PhD candidate.

The Key Laboratory of Road and Traffic Engineering, Tongji University, Shanghai 201804, China

Email: sunshine20515@yeah.net

ABSTRACT

Highly modified asphalt binders have become the preferred choice for high-grade flexible pavements; however, current research lacks clarity on the mechanisms of short-term oxidation and degradation among different modifiers. In response, this study investigates the short-term aging of various modified asphalt binders, including SBS, crumb rubber, PPA, and gilsonite. The study utilizes a PG 58-22 neat asphalt and eight modified binders, examining their aging behavior at temperatures of 163°C, 178°C, and 193°C. The study utilizes FTIR, oscillation tests, Multiple Stress Creep Recovery (MSCR), and master curve techniques to analyze the binders post-aging. Results show that PPA reduces aging by preventing asphaltenes micelle agglomeration, whereas other modifiers show increased aging and carbonyl formation. Gilsonite-modified binders exhibit the least aging resistance, while CR and SBS display softening effects with stable modulus post-aging. Higher modifier dosages (20% CR, 24% Gilso, 7.5% SBS) reduce aging severity by increasing viscosity, which limits the flow and reduces oxidation and volatilization within the RTFOT.

Keywords: Modified asphalt, short-term aging, oxidation, polymer, chemical properties, master curve.

1 Introduction

Asphalt modified with polymers (PMA) has become a prevalent choice in the development of high-quality flexible road surfaces, primarily because of its excellent elastic properties and its resistance to deformation [1,2]. As the traffic load on highways keeps increasing, there is a growing trend of using higher dosages of polymer modification to achieve overall better road performance [3,4].

Highly modified asphalt often exhibits non-Newtonian characteristics and elevated viscosity, which are key factors contributing to its enhanced mechanical properties [5,6]. However, this increased viscosity can pose challenges in conventional experiments that are designed for unmodified neat asphalt with lower viscosities. For example, the Rolling Thin Film Oven Test (RTFOT) is a widely used method to simulate the short-term aging process of asphalt binders during mixing, transportation, and compaction [7,8]. RTFOT was introduced by the California Department of Transportation in 1963 and has been successfully used for several decades, becoming part of both AASHTO and ASTM standards [9]. However, RTFOT has been reported unsuitable for PMA due to the insufficient fluidity problem of high viscosity PMAs.

RTFOT requires that 35g of asphalt binders to spread evenly inside an aging bottle to form a thin asphalt film of 5~10 μm [10]. This small film thickness notably accelerates the aging process, making an 85-minute RTFOT aging treatment equivalent to a 5-hour Thin Film Oven Test (TFOT) aging treatment [11]. According to the AASHTO T240, RTFOT should be conducted at 163℃, which is a representation of the field conducting temperature of neat asphalt. Obviously, this temperature might be too low for PMA, especially highly modified ones [12]. At 163℃, these binders cannot gain enough fluidity to achieve satisfactory film thickness, leading to insufficient aging severity after RTFOT aging.

In response, numerous methods have been introduced to simulate the short-term aging of PMA [13]. Nevertheless, these aging techniques have not become widely adopted due to the financial and practical challenges of replacing existing equipment. Bahia [14] previously attempted to enhance RTFOT by incorporating a steel rod or several steel spheres into the glass aging bottle to generate additional shear forces and improve the spreading of the thin film.

Others tried to adjust the testing parameters of RTFOT to make it more suitable for PMA and other highly modified asphalts [15]. The most commonly utilized strategy is increasing the aging temperature. The increase varies from 10℃~30℃ and results in notably enhanced aging severity [16]. In a previous study [17], the authors have discussed the influence of temperature on the aging severity of SBS modified asphalt binders. It is found that the RTFOT for SBS modified asphalt should be elevated to 178℃ or even 193℃, depending on the SBS dosage.

With the advance of asphalt modification technology, an increasing number of modifiers are used in the field other than SBS elastomer [18]. Some of the most commonly used ones are crumb rubber (CR), EVA and gilsonite. All of them are considered to benefit the asphalt rutting resistance and more cost-friendly than SBS modifiers. Additionally, certain small-molecule organic materials, including polyphosphoric acid (PPA) and paraffin wax, have also been extensively utilized as modifiers [19].

To study the oxidation and degradation mechanisms in the short-term aging of mainstream asphalt modifiers, this research examines the aging behavior of commonly used modifiers like CR, PPA, and gilsonite. To achieve this goal, a PG 58-22 neat asphalt and 8 modified asphalt binders with different formulas are subjected to RTFOT aging. After aging, the residue was characterized using FTIR, oscillation test, Multiple Stress Creep Recovery (MSCR) test and master curve. Finally, by correlation the FTIR results with rheology testing results, the influence of short-term aging on the viscoelastic characteristics and elastic responses are investigated.

2 Material and testing methods

2.1 Materials

Four most commonly employed modifiers (SBS, gilsonite, CR, and PPA) were selected to modify a PG 58-22 neat asphalt. For each modifier, two dosages are examined and they are based on common industrial selections. Table 1 presents the basic properties of the neat asphalt and modifiers, while Table 2 lists the dosages of various modifiers, expressed as a percentage of the neat asphalt's weight. The dosage of the modifiers was determined according to the recommended amounts for commercially available modified asphalt.

For the preparation of PPA and gilsonite-modified asphalt, the neat asphalt was first heated to 165°C, after which the appropriate amount of modifier was introduced. The blend was then subjected to shearing at 5000 rpm for 30 minutes, followed by stirring at 1000 rpm for an additional 120 minutes at the same temperature to ensure uniform distribution of the modifiers.

Due to the higher molecular weight and more complex molecular structure of SBS and CR modified asphalts, which exhibit poorer compatibility, we referred to our previous research [20]. The temperature of the neat asphalt was raised to 180°C, and the shearing time was extended to 120 minutes to ensure sufficient shearing and swelling.

2.2 Laboratory aging

RTFOT was selected to simulate the short-term aging in the lab. Due to the increased viscosity of many modified asphalts, especially highly modified ones, the asphalt applying temperatures are also being elevated. To simulate the more serious short-term aging at elevated temperatures, the aging temperatures were set to 163°C, 178°C and 193°C with a 15°C gap. The aging period remained 85 min according to AASHTO T240. Different aging sessions are coded as R163, R178 and R193, respectively.

2.1 FTIR

The asphalt samples were analyzed using a Bruker TENSOR infrared spectrometer to assess aging by examining changes in the peak areas of carbonyl and sulfoxide groups. However, due to the instability of sulfoxide groups at high temperatures, which leads to degradation, only the carbonyl index was used to evaluate asphalt oxidation.

2.2 Dynamic shear oscillation test

The dynamic shear oscillation test were conducted using a DHR-3 dynamic shear rheometer (DSR) in accordance with the AASHTO T 315 standard [21].

2.3 Multiple Stress Creep and Recovery (MSCR) test

The MSCR test was conducted in accordance with AASHTO TP-70-13 [22], with the final average elastic recovery and non-recoverable compliance calculated as evaluation indicators [23].

2.4 Master Curve

In this study, a temperature range of 5°C to 75°C was selected, with 10°C intervals, and the frequency sweep was determined to range from 0.1 to 30 Hz. To ensure testing accuracy, different diameters of parallel plates were used at different test temperatures: an 8 mm diameter plate with a 2 mm gap was employed for temperatures below 35°C (i.e., 5°C to 25°C), while a 25 mm diameter plate with a 1 mm gap was used for temperatures above 35°C (i.e., 35°C to 75°C) [24,25]. The master curve was constructed using the sigmoidal master curve model, with 25°C as the reference temperature [17,26].

2.5 TLC-FID test

The Thin-layer Chromatography with Flame Ionization Detection (TLC-FID) method was utilized to test different binders. Firstly, dichloromethane is mixed with asphalt at a ratio of 1:10 to achieve dissolution. The completely dissolved asphalt solution is then applied in dots on the chromarod. Subsequently, the chromarod is developed sequentially with n-heptane, toluene/n-heptane, and dichloromethane/methanol, followed by drying to remove the developer. Finally, the chromarod is placed on the scanning platform and passed through a hydrogen flame at a rate of 30 seconds per rod. The area under the curve obtained represents the proportion of the four components.

3 Results and Discussion

3.1 Infrared spectra

Infrared spectra were recorded for different modified asphalts and the results of SBS, PPA, CR and Gilso modified asphalt binders are shown in Figure 1 to 4. To highlight the change in carbonyl and thus assess the aging severity, the X-axis is set to 1400 cm^{-1} ~1900 cm^{-1}

Seen from Figure 5, increasing the aging temperature enhances the carbonyl generation for all modified binder, indicating a severer aging level. It seems that PPA can strength the aging resistance of asphalt and suppress the carbonyl generation. This is consistent with related studies that demonstrate PPA modification can retard the aging of asphalt binder. Lining's study suggest that this might be due to the PPA's ability to disperse the asphaltenes micelle from agglomeration [27].

Introducing a low content of CR (CR10), Gilso (Gilso12) and SBS (SBS45) appears to promote the aging behavior as well as the carbonyl generation. This might be because that these modifiers contain considerable active functional groups that are susceptible to oxidation. However, it is also observed that a higher dosage of these modifiers (CR20, Gilso24, SBS75) results in a smaller carbonyl generation compared to lower dosages.

This counterintuitive observation is believed to be explained by the higher modifier dosage, leading to an increased viscosity, which hinders the fluidity of asphalt inside the RFTOT aging bottle and weakens the aging effects. The SBS75 sample tested in this study has a very high viscosity and is usually used for open-graded drainage pavement. With such a high viscosity, SBS75 demonstrates almost zero carbonyl generation after 163°C RTFOT aging. It is also noteworthy that CR20 shows small carbonyl growth after aging of all three temperatures. Unlike other modifiers, CR modifier has a unique chemical cross-linked molecular structure and will not melt or soften at high temperatures, as a consequence, CR20 retains a high viscosity even at 193°C, limiting the effectiveness of RFTOR aging.

3.2 Modulus obtained from oscillation test

According to Figure 6, all modifies stiffen the modified binder and elevated testing temperature always leads to reduced modulus. At a conventional dosage, Gilso-modified binder showed the greatest modulus increase, followed by PPA, CR and SBS. The increase caused by aging was less evident for CR and SBS. Notably, SBS75's modulus barely changes after RTFOT aging (regardless of the aging temperature).

The stability in modulus of CR and SBS modified asphalt before and after aging is ascribed to the softening effects of polymer degradation [28]. Polymers, especially elastomers like CR and SBS, have a long-chain molecular structure that provides the material with outstanding elasticity and strength. However, these long-chain structures are usually vulnerable to heat or oxidation and may degrades confront such extreme conditions. Degraded polymer usually shows reduced modulus, this may compensate or counteract the modulus increase caused by hardening of neat asphalt, resulting in a relatively stable modulus before and after aging [29].

3.3 Phase angle obtained from oscillation test

According to Figure 7, all modifies have enhanced the elasticity of asphalt binders and have lowered the phase angle value. At a intermediate dosage, SBS polymer showed the greatest modifying effects, followed by CR, Gilso and PPA. In terms of aging, it was quite interesting that SBS and CR exhibited increasing phase angle value after aging, which was opposite to that observed for neat binder, PPA and Gilso. As mentioned before, the elasticity provided by SBS and CR was primarily contributed by their crosslinked molecular network. However, thermal aging significantly damages this chemical crosslinked network, leading to a reduction in the elastic behavior of these asphalt binders. This degradation is reflected in increased phase angles after aging, indicating a less-elastic response of the modified asphalt binders.

To further facilitate the understanding of how aging influence the linear viscoelasticity (both modulus and phase angle) of various modified asphalt, the correlation between carbonyl growth and complex modulus as well as phase angle are presented in Figure 8. It can be seen that Gilso12 shows the least aging resistance as it exhibits the maximum carbonyl growth after aging, it also demonstrates a noticeable modulus growth as well as a phase angle reduction, indicating its sensitivity to aging. PPA modified asphalt binders shows the least carbonyl generation, but CR and SBS modified asphalt binders show a more stable modulus evolution along with aging (represented by carbonyl growth). They also even show an increased phase angle with increased aging severity.

3.4 R3.2 obtained from the MSCR test

The R3.2 of modified binders were presented in Figure 9. SBS, CR and Gilso had significantly increased the R3.2 of modified asphalt binders while PPA seemed to have little impact on R3.2. This is expected due to the small molecular weight of PPA and its relatively low dosages. For practical application, the dosage of PPA cannot be too high because it will easily lead to the gelation of asphalt binders [30].

In terms of aging, it was found the growing aging severity will increase the R3.2 of neat binder, PPA and Gilso. On the other hand, aging will lower the R3.2 of CR and SBS-modified binders. This phenomenon was quite similar to what observed for phase angle and could also be explained be the interplay between asphalt hardening and polymer degradation happened during aging. On one hand, aging stiffens the asphalt phase and thus increase the elasticity of neat binder, PPA and Gilso, on the other hand, elastomers like CR and SBS degrades, hence reducing the elasticity of corresponding modified asphalt binders.

The correlation between R3.2 and phase angle measurements (measured at 76℃)

is shown in Figure 10. For most modified binders (except SBS-modified binder), there was a linear correlation between the binder's R3.2 and phase angle value, irrespective of the modifier dosage or aging level. This correlation is understandable as both R3.2 and phase angle are indicators of the asphalt binders' elastic behavior.

It is noteworthy that SBS75, owing to its exceptional elasticity, consistently shows a high R3.2 value (>80%) at all aging conditions. Therefore, its R3.2 was not linear correlated with phase angle because R3.2 has an upper limit of 100%.

Also, it was seen that depending on the variance of modifier type and modifier dosage, R3.2 varied between 0% to 100% while phase angle only varied between 40° to 90°. The greater change amplitude of R3.2 suggested that R3.2 was more sensitive to the introduction of modifier and may serve as a better indicator to quantify the elastic behavior of modified asphalt binders.

3.5 Jnr3.2 obtained from the MSCR test

The Jnr3.2 is calculated to evaluate the rutting resistance of modified binders. Based on the Jnr results from Figure 11, Figure 12 shows the correlation between Jnr3.2 and modulus (at 76°C).

It was interesting to see that at a logarithmic scale, neat binder, PPA and Gilso-modified binders exhibited a linear negative correlation between Jnr3.2 and complex modulus, which means for these binders, the effects of asphalt-phase hardening predominates and thus the rutting resistance improves with aging severity.

However, the opposite was found for CR and SBS-modified binders. As their

Jnr3.2 and modulus show a positive correlation. As discussed in Figure 9, aging will also lead to the degradation of SBS polymer and CR, resulting in deteriorated elasticity and possible more viscous deformation. This means weakened rutting resistance and generally lower Jnr3.2 values.

From this point of view, in terms of quantifying the rutting performance of PMA, Jnr3.2 might be a better indicator than complex modulus or rutting parameter ($G^*/\sin\delta$) because it was more sensitive to polymer degradation and will not overestimate the influence of the hardening of asphalt phase.

3.6 Master curve

To assess the change in viscoelasticity happened during the aging process, master curves are constructed before and after different aging treatments. The master curves for neat asphalt and different modified asphalts are shown in Figure 13.

The modulus increase at 10^{-5} Hz was highlighted in the graph using a red line, providing a visual representation of the aging effects on the linear viscoelasticity. A lower frequency (10^{-5} Hz) is chosen because at high frequencies, all asphalt binders enter the glassy stage and show a glassy plateau modulus of 10^9 Pa [31], rendering the effects of aging insignificant.

By looking at the length of the red line, it can be seen that compared with unmodified neat asphalt, all modified asphalt binders show a more stable viscoelasticity during aging, particularly the highly modified ones. SBS and CR modified asphalts are the most stable ones, with CR20 and SBS75 showing almost overlapped master curves for different aging conditions. As mentioned before, this is attributed to the interplay between asphalt hardening and polymer degradation.

PPA and Gilso do not possess a long-chain molecular structure and thus do not show any softening after aging, resulting in greater modulus increase compared to SBS and CR. But as indicated by the infrared spectra analysis, PPA seems to be able to retard the asphalt aging by dispersing the asphaltenes micelle from agglomeration. Therefore, PPA shows slightly alleviated aging than Gilso. Gilso does not have a long-chain molecular structure nor unique chemical characteristics to retard the aging, and thus shows the most obvious modulus increase after aging (except neat asphalt).

3.7 Effect of ageing temperature on SARA fractions of asphalt binder

The research presented in previous sections indicates that increasing the dosage of modifiers leads to a rise in viscosity, which in turn hinders the flow of asphalt within the RTFOT aging bottle, thus diminishing the aging effect. This section aims to explore how the composition of high-viscosity modified asphalt changes within the RTFOT after the short-term aging temperature is elevated. To this end, TLC-FID tests were conducted on neat asphalt, PPA2.0, Gilso24, and SBSs75.

The chemical reactions involved in the asphalt aging process are highly complex. It is generally believed that the saturated components are relatively stable, while the aromatic components can undergo oxidation or polymerization reactions to produce asphaltenes and resins, with resins being transformed into asphaltenes through polymerization and condensation actions.

As illustrated in Figure 14, with the aging temperature increasing from 163°C to 193°C, the content of saturates and aromatics in neat asphalt decreases while resin and asphaltenes increase. This indicates that the rise in aging temperature accelerates the transformation of light constituents into heavy constituents. This acceleration is likely due to the promotion of volatilization or oxidation reactions of light components at higher temperatures. In the case of modified asphalt, raising the aging temperature also accelerates the increase in heavy components. However, the difference between 163°C and 178°C is relatively minor, especially for CR20 and SBS75. This may be because the temperature of 178°C is not sufficient to allow high-viscosity asphalts to flow adequately. The noticeable reduction in light components when the aging temperature reaches 193°C confirms this observation.

4 Conclusion

- Infrared spectra analysis indicates that PPA can strength the aging resistance of asphalt and suppress the carbonyl generation. This is attributed to its ability to disperse the asphaltenes micelle from agglomeration. On the other hand, introducing a relatively low content of CR (10%), Gilso (12%) and SBS (4.5%) promotes the carbonyl generation during aging, as these modifiers contain considerable active functional groups.
- A higher dosage of modifiers (20%CR, 24%Gilso, 7.5%SBS) results in a reduced carbonyl generation during laboratory aging. This is because a higher modifier dosage leading to an increased viscosity, which hinders the fluidity of asphalt

inside the RFTOT aging bottle and weakens the aging effects. From this aspect, the laboratory aging temperature for highly modified asphalt binders should be increased.

- Gilso modified asphalt binder shows the least aging resistance as it exhibits the maximum carbonyl growth with noticeable modulus/phase angle variations. CR and SBS modified asphalt binders show the best aging resistance. They demonstrate less modulus evolution along with aging and they even show increased phase angle values with increased aging severity, which are due to the damage of their elastic polymer network during aging.
- The aging behavior of CR and SBS contains two parts, which is asphalt hardening (oxidation) and polymer degradation. While asphalt hardening renders the binder stiffer, the polymer degradation makes the binder more viscous, and thus, the viscoelastic properties of PMA are a combined result of both processes. This is confirmed in all of oscillation test, MCSR test and master curves. CR20 and SBS75 showing almost overlapped master curves for different aging conditions.
- The results of SARA tests demonstrate that increasing the aging temperature significantly facilitates the transformation of light constituents into heavy constituents in asphalt.

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Table captions

Table 1 Information of asphalt binder

Table 2 Examined asphalt binders and their code name used in this study

Figure captions

Figure 1. FTIR result for SBS modified asphalt (both and SBS75 and SBS45)

Figure 2. FTIR result for SBS modified asphalt (both and PPA2.0 and PPA0.8)

Figure 3. FTIR result for SBS modified asphalt (both and CR20 and CR10)

Figure 4. Infrared spectra for SBS modified asphalt (both and Gilso12 and Gilso24)

Figure 5. Calculated carbonyl index based on the infrared spectra

Figure 6. Modulus evolution along with aging (64℃~82℃)

Figure 7. Phase angle evolution along with aging (64℃~82℃)

Figure 8. Correlation between carbonyl and (a) modulus and (b) phase angle measured at 76℃

Figure 9. R3.2 results obtained from the MSCR test (64℃~82℃)

Figure 10 Correlation between R3.2 and phase angle (measured at 76℃)

Figure 11. Jnr3.2 results obtained from the MSCR test (64℃~82℃)

Figure 12. Correlation between Jnr3.2 and modulus presented (measured at 76℃)

Figure 13. Master curve for neat asphalt and modified asphalt

Figure 14. SARA of Binders in different aging temperatures

Table 1 Information of asphalt binder

Item	Information
Neat asphalt	PG 58-22 unmodified petroleum asphalt
Gilsonite	asphaltene content: 98.4%, ash content: 0.72%
PPA	P_2O_5 content: 85%
SBS	791-H linear SBS polymer, S/B: 30/70
Crumb rubber	30 mesh, natural/synthesis rubber content: 54%

Table 2 Examined asphalt binders and their code name used in this study

Modifier	Dosage	Code name
SBS	4.5 wt. %	SBS45
	7.5 wt. %	SBS75
Gilsonite	12 wt. %	Gilso12
	24 wt. %	Gilso24
Crumb rubber	10 wt. %	CR10
	20 wt. %	CR20
PPA	0.8 wt. %	PPA0.8
	2.0 wt. %	PPA2.0

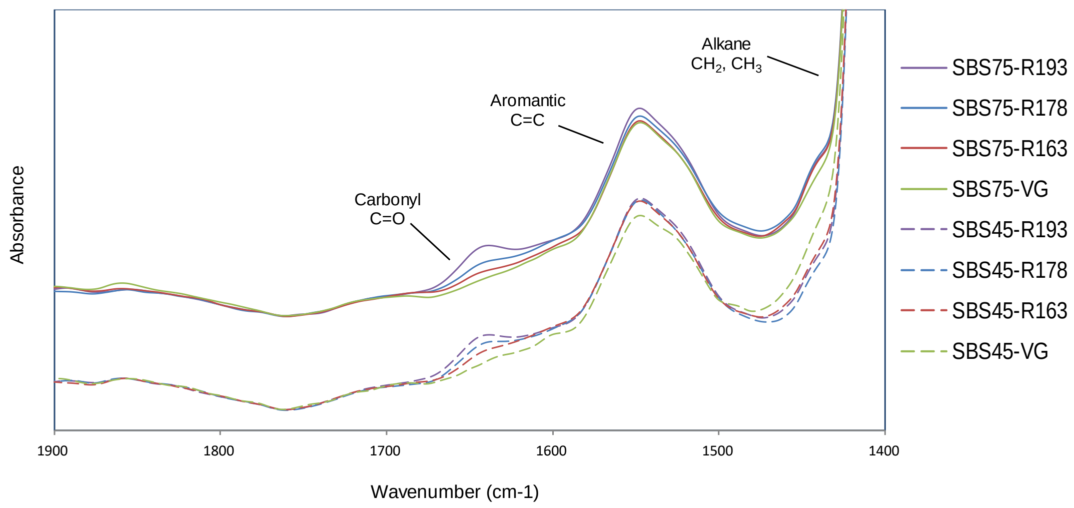


Figure 1. FTIR result for SBS modified asphalt (both and SBS75 and SBS45)

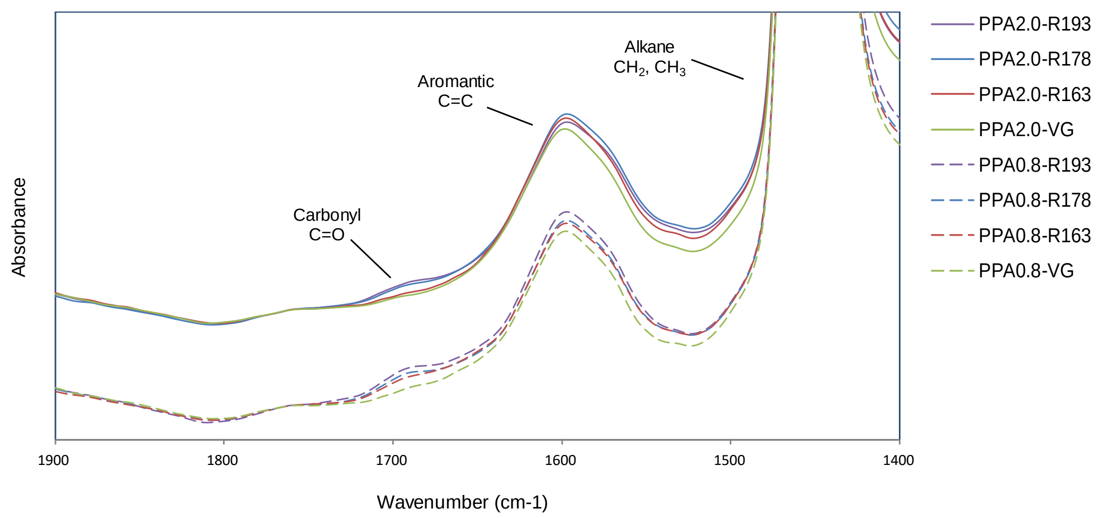


Figure 2. FTIR result for SBS modified asphalt (both and PPA2.0 and PPA0.8)

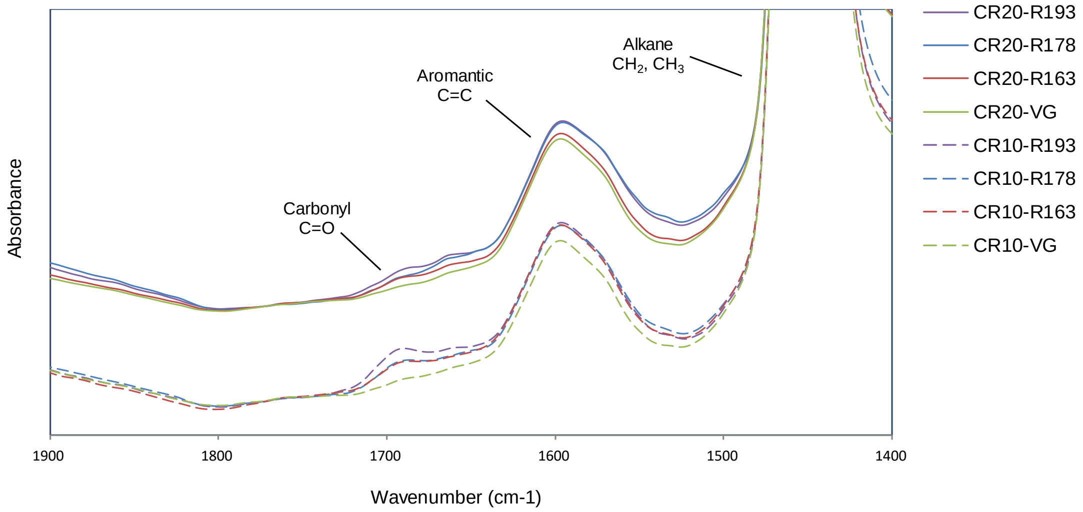


Figure 3. FTIR result for SBS modified asphalt (both and CR20 and CR10)

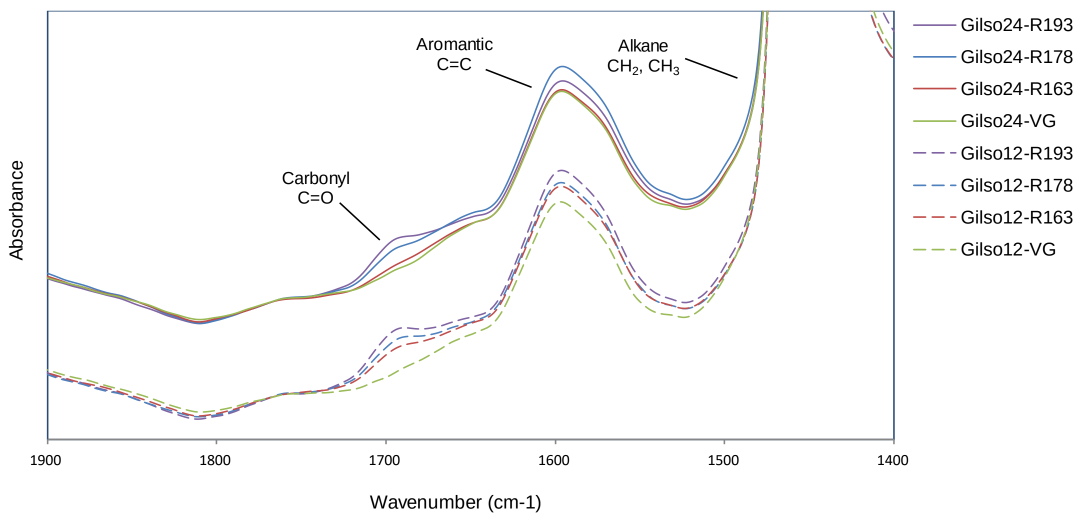


Figure 4. Infrared spectra for SBS modified asphalt (both and Gilso12 and Gilso24)

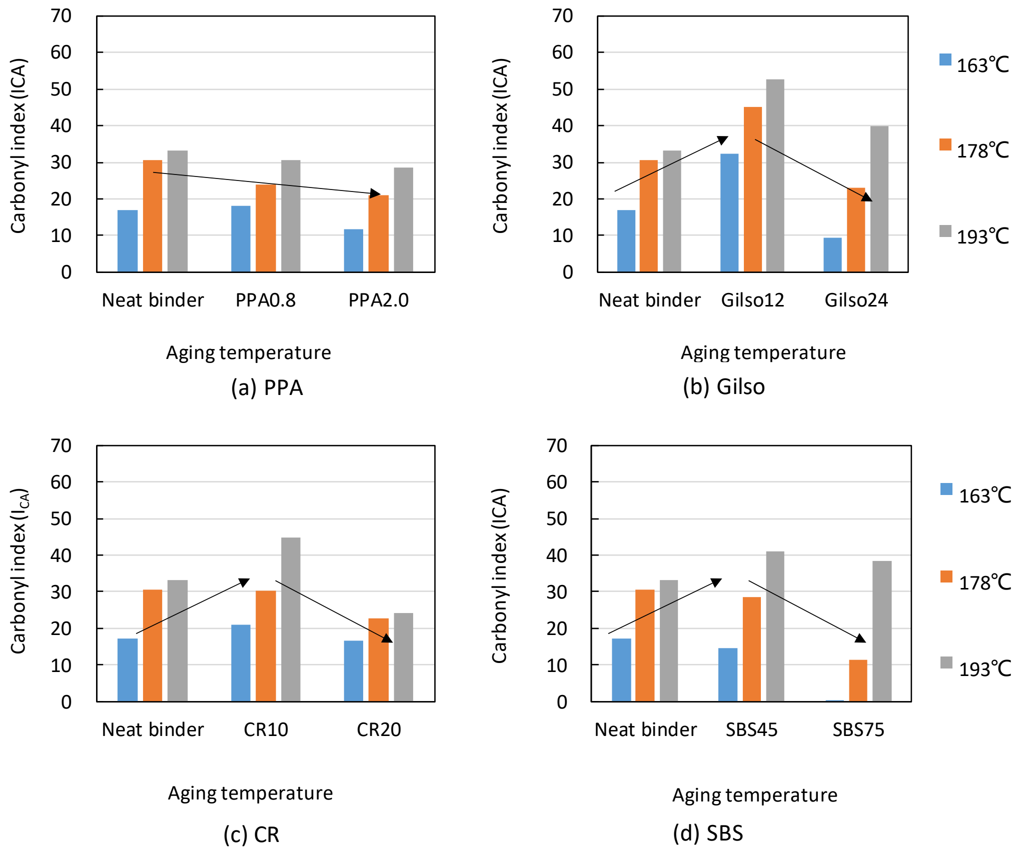
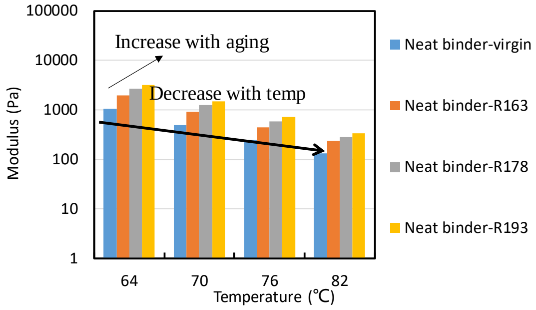
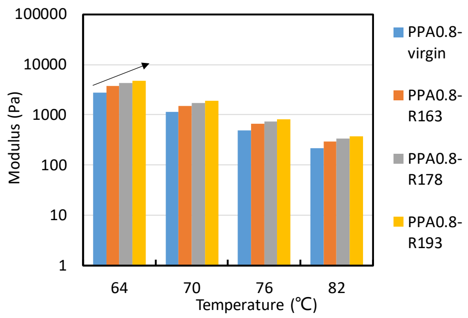


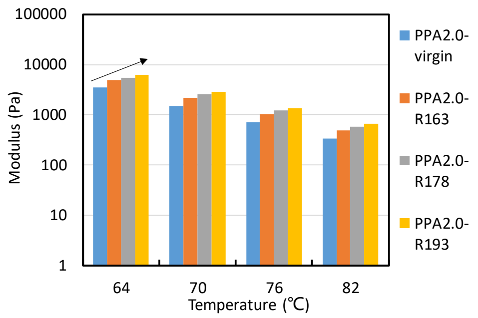
Figure 5. Calculated carbonyl index based on the infrared spectra



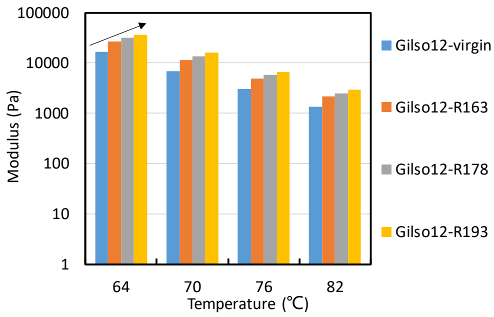
(a) Neat asphalt



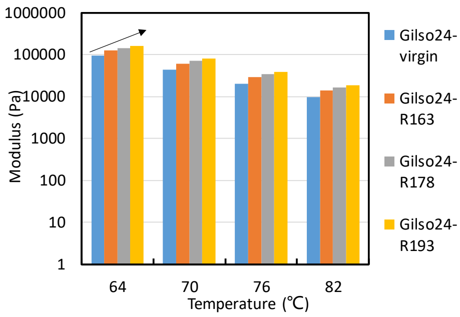
(b) PPA0.8



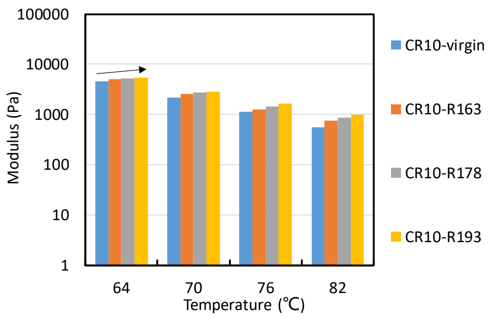
(c) PPA2.0



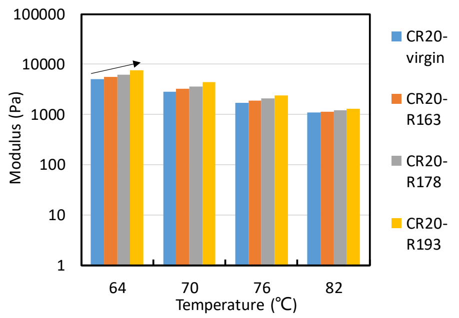
(d) Gilso12



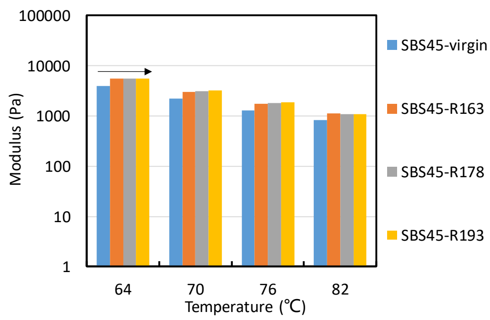
(e) Gilso24



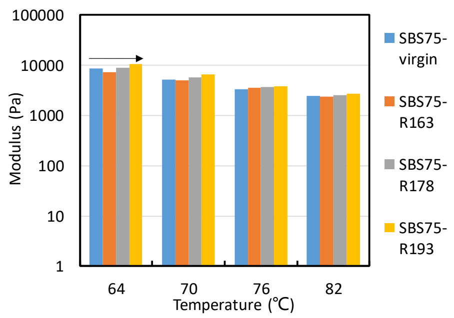
(f) CR10



(g) CR20



(h) SBS45



(i) SBS75

Figure 6. Modulus evolution along with aging (64℃~82℃)

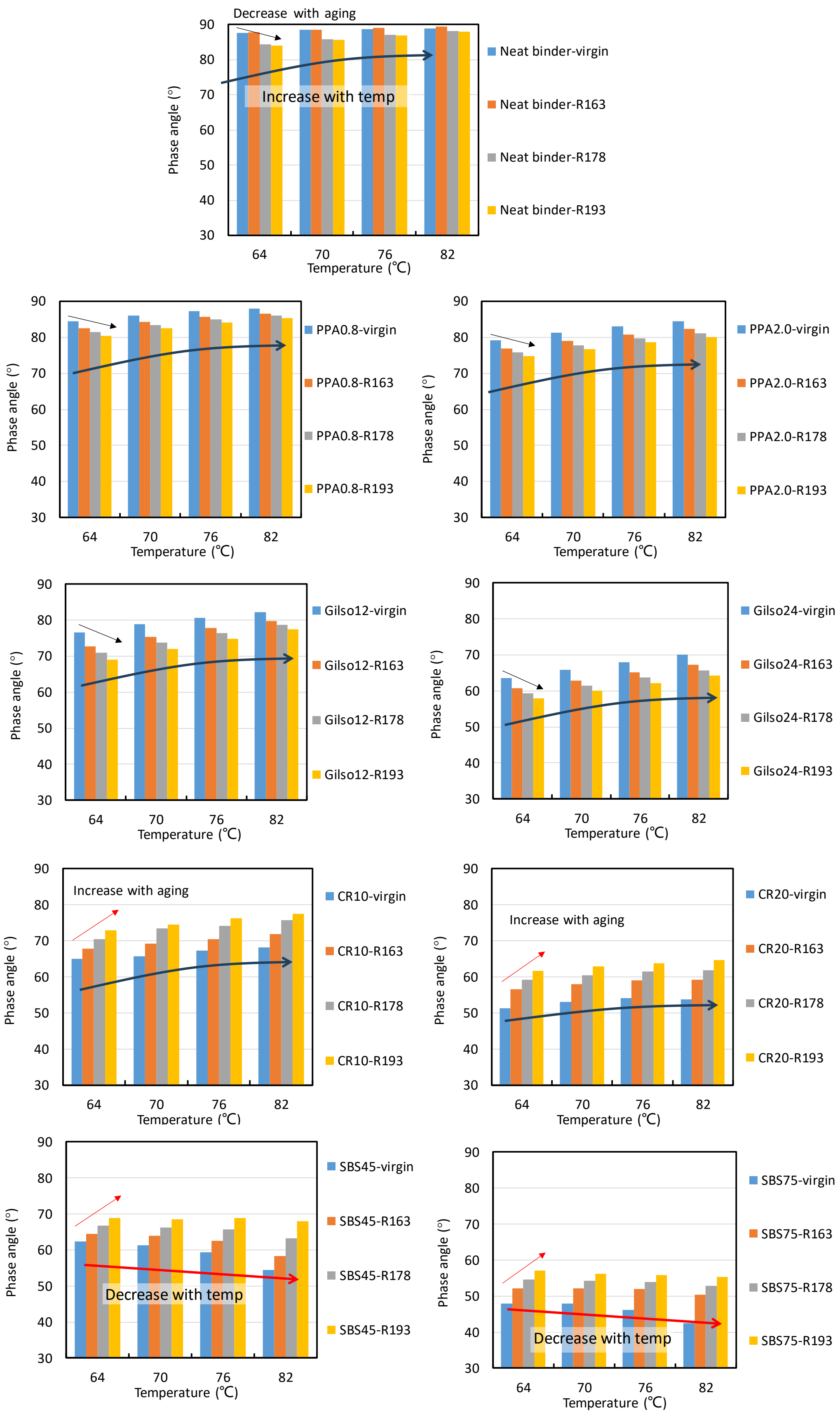


Figure 7. Phase angle evolution along with aging (64℃~82℃)

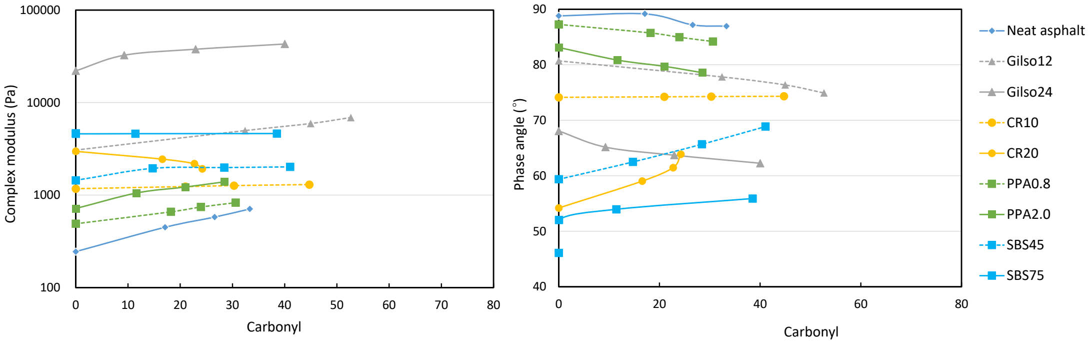


Figure 8. Correlation between carbonyl and (a) modulus and (b) phase angle

measured at 76℃

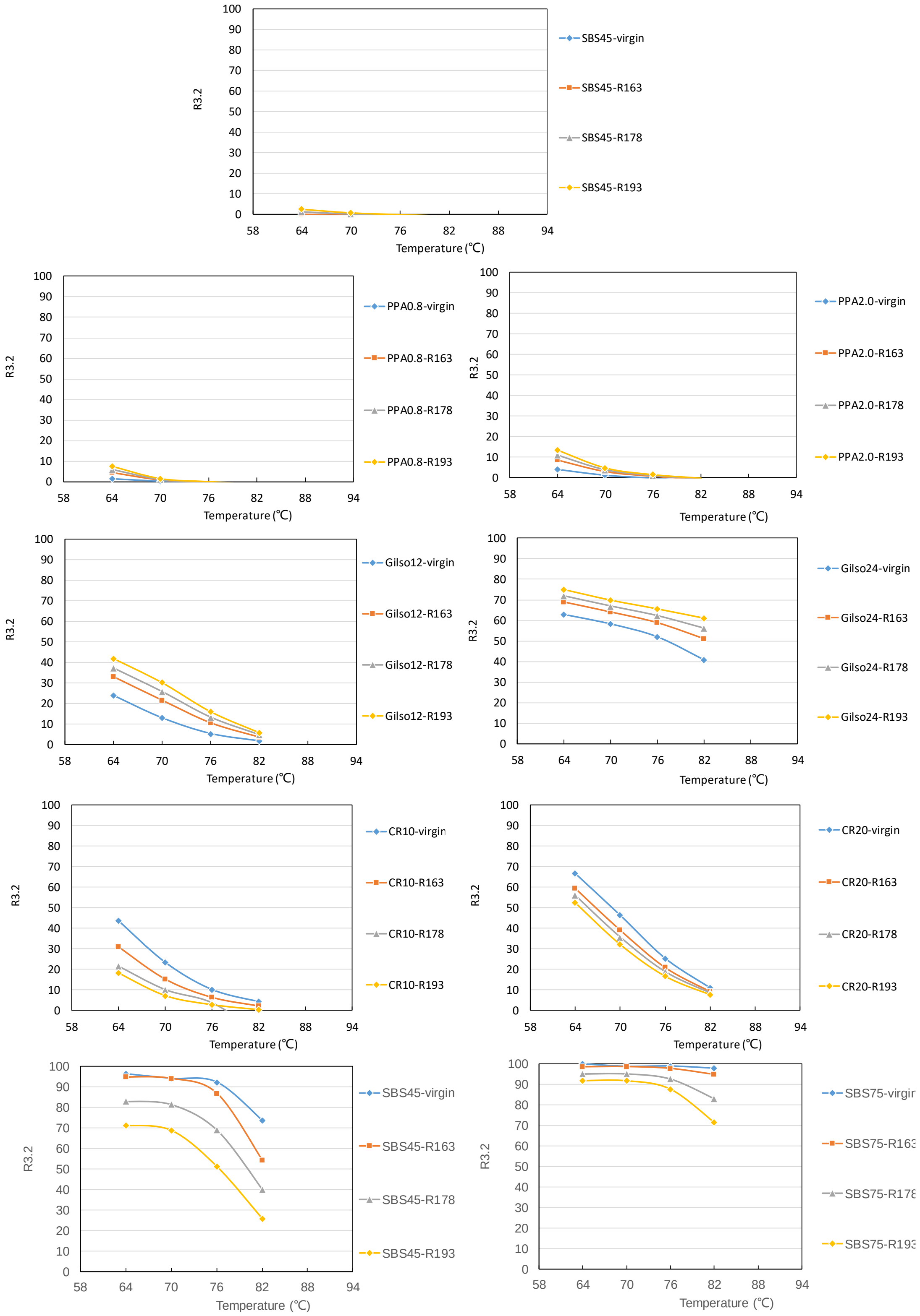


Figure 9. R3.2 results obtained from the MSCR test (64℃~82℃)

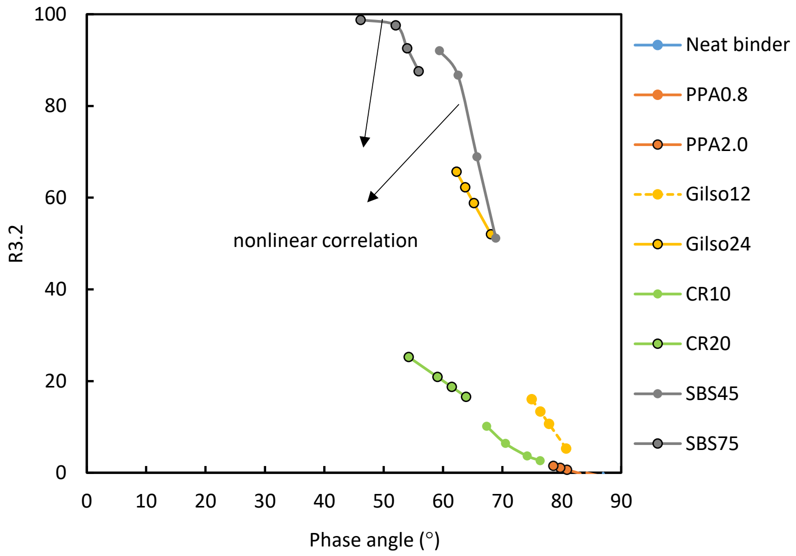


Figure 10 Correlation between R3.2 and phase angle (measured at 76°C)

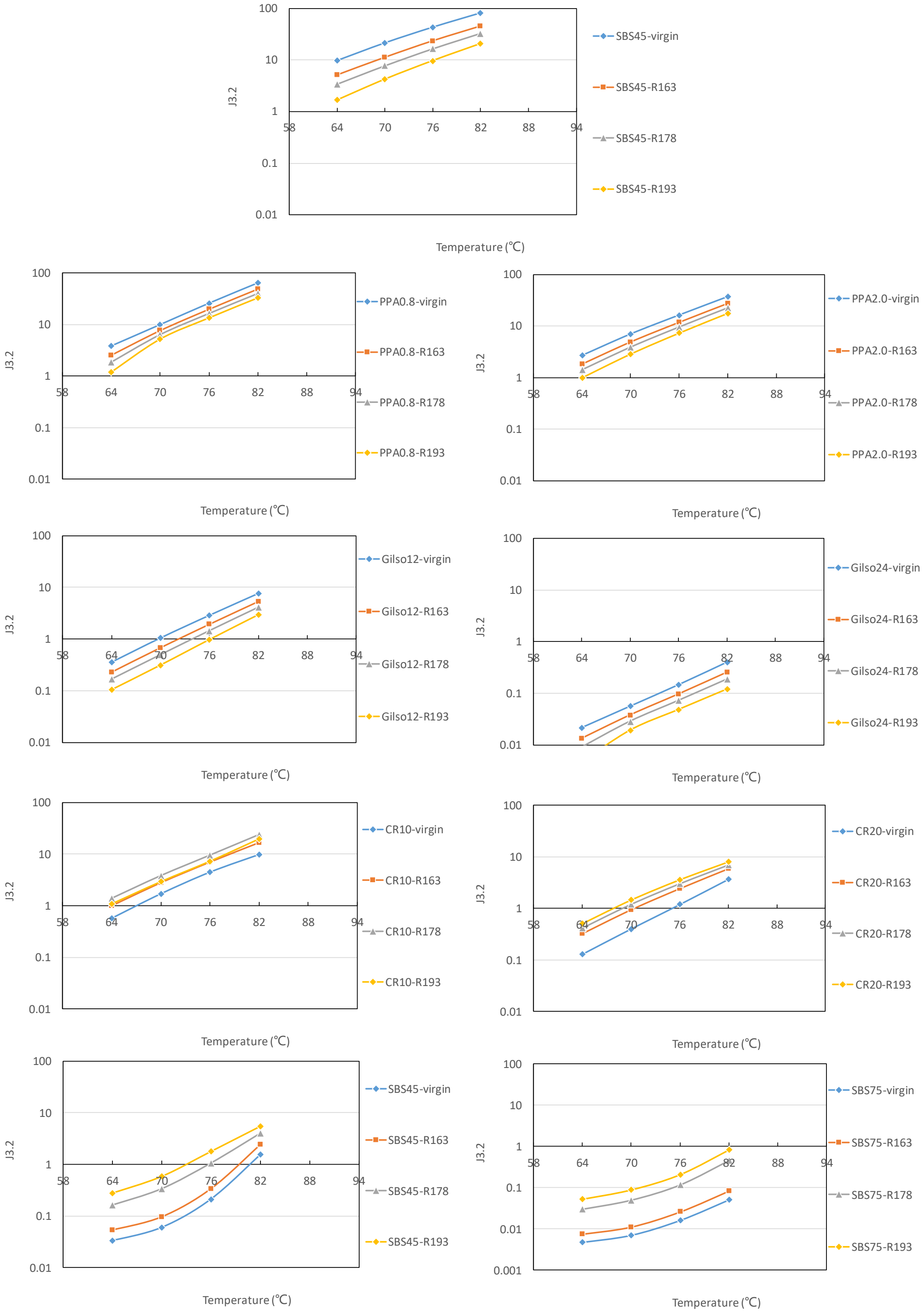


Figure 11. Jnr3.2 results obtained from the MSCR test (64℃~82℃)

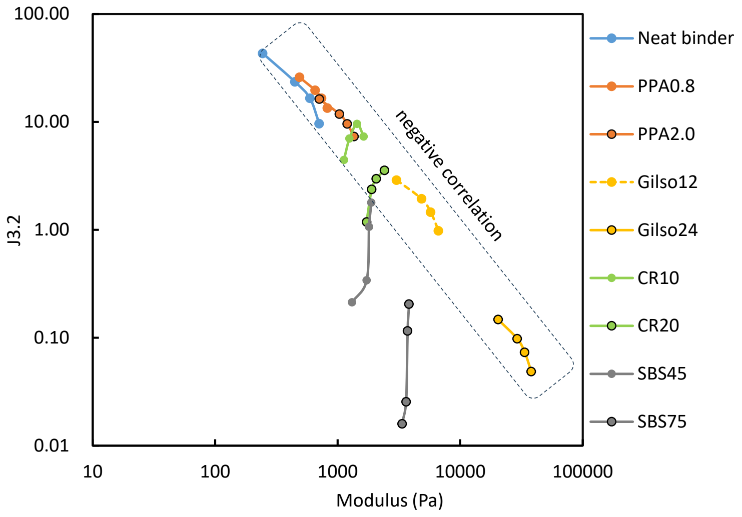


Figure 12. Correlation between Jnr3.2 and modulus presented (measured at 76°C)

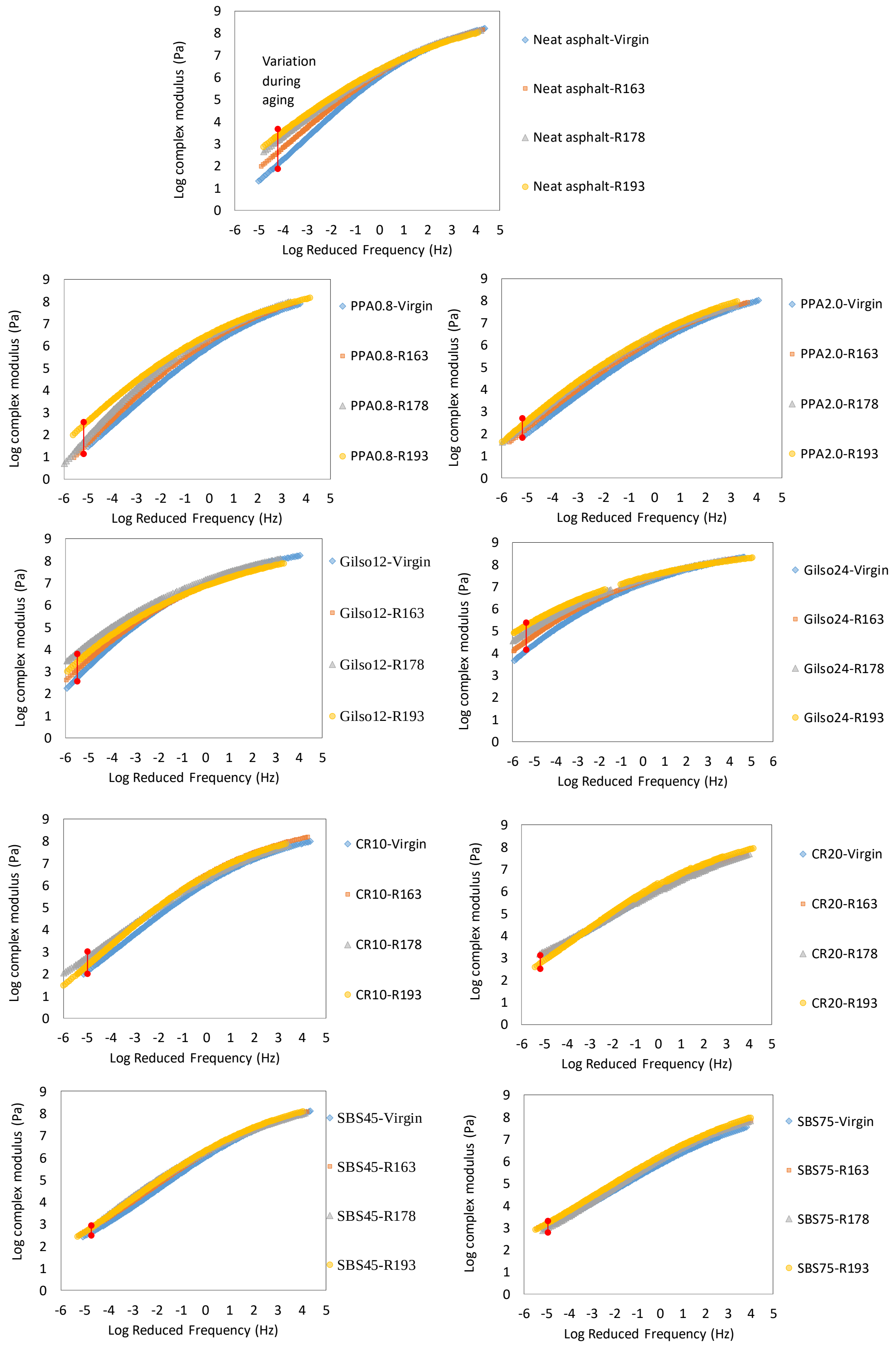


Figure 13. Master curve for neat asphalt and modified asphalt

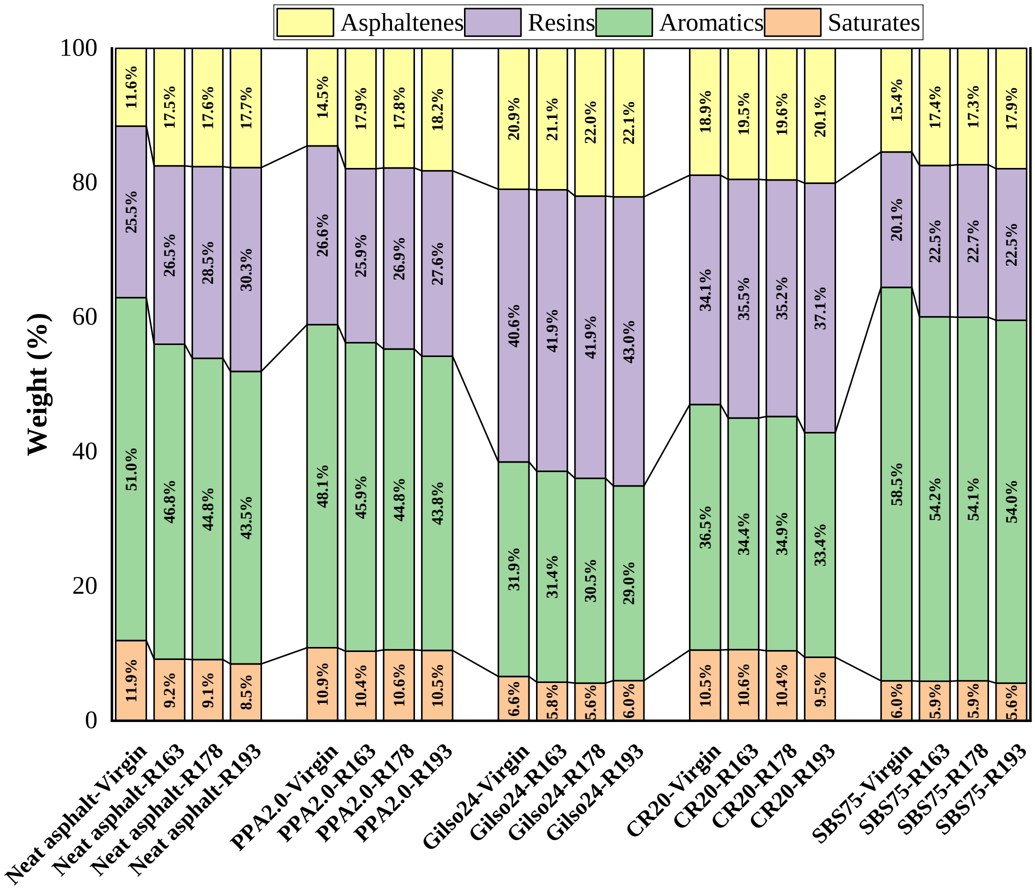


Figure 14. SARA of Binders in different aging temperatures

Quan Lv received his PhD of Road Engineering from Tongji University in 2018. He is an associate research fellow in Road Engineering at the College of Transportation Engineering of Tongji University. His areas of research focus on highly modified asphalt, adhesion property of asphalt binder and crumb rubber modified asphalt.

Jie Gao received her master's degree of Communication and Transportation Engineering from Tongji University in 2022.Currently, she is a road engineering designer at Beijing Municipal Engineering Design and Research Institute Co., Ltd. Her areas of research include road alignment design and asphalt pavement design.

Shaopeng Liu received his MSc degree of Transportation Engineering from Tongji University. He is an engineer at the Transport Planning and Research Institute, Ministry of Transport. His areas of research include highway engineering management, subgrade engineering, pavement structure and materials.

Chuanqi Yan received his PhD in Road Engineering from Tongji University in 2020. He is an associate professor in Road Engineering at the College of Transportation of Southwest Jiaotong University and a master's student supervisor. His areas of research focus on high-performance modified asphalt materials and their characterization and development.

Haixiao Hu received her Master degree in Transportation Engineering from Southeast University in 2016. Received her Bachelor degree in Civil Engineering (Road and Bridge) from Jilin University in 2013. She is working at Shandong Provincial Communications Planning and Design Institute Group Co.,Ltd, mainly engaged in roadbed and pavement design work.

Liyuan Liu received his PhD of Road Engineering from Tongji University in 2024. His areas of research focus on polymer modified asphalt.