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Aging and rejuvenation effects on the rheological response and chemical parameters of bitumen

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ABSTRACT

The rejuvenation efficiency of aged bitumen is the main concern when developing rejuvenating agents. It is necessary to develop a method to assess the efficiency of rejuvenators using rheological parameters in the whole frequency region. To this end, the 2S2P1D micromechanics model is adopted to fit the entire G* master curves of various rejuvenated bitumen, and the influence of rejuvenator type/dosage and aging grade of bitumen on the whole G* master curve and chemical indices are investigated. Critical parameters for evaluating rejuvenation efficiency derived from viscoelastic models and chemical characterizations are proposed. Furthermore, the potential relationships between the rheological model-based parameters (E_∞, δ, β, and τ) and chemical indices (carbonyl index CI and sulfoxide index SI) are explored. The results indicate that rejuvenators restore the δ, τ, CI, and SI values of aged bitumen towards the virgin bitumen level. The E_∞ parameter is not applicable to evaluate the rejuvenation efficiency of engine-oil and naphthenic-oil rejuvenators, but the positive $E_\infty R$ values of bio-oil and aromatic-oil rejuvenated bitumen are detected. All rejuvenators fail to restore the β parameter of aged bitumen. The τ and CI parameters are selected as critical evaluation indicators from the perspective of viscoelastic models and chemical characteristics. Linear correlations between all rheological parameters and chemical indices are observed and established.
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1. Introduction

Asphalt concrete for flexible pavements is one of the most widely used materials in the construction industry. Annual worldwide production of asphalt mixtures for paving operations has been estimated to be more than one billion tons [1]. Given that flexible pavements consume huge amounts of aggregates and bitumen binders, efforts to produce sustainable pavements have led to using alternative materials in the paving industry [2]. During the pavement service life, asphalt mixtures are subjected to traffic loading and environmental conditions such as moisture, temperature variation, and air contact, which could lead to some permanent distresses of the pavement such as rutting, ravelling, cracking, etc. [3,4].

Removal of old asphalt pavement produces a huge amount of reclaimed (RAP) materials [5]. There are about 47 and 72.5 million tons of RAP waste materials in European and United States, respectively [6]. Using RAP materials in new paving applications is valuable for conserving natural resources and

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reducing environmental problems. Nowadays, many highway and transportation agencies permit the use of RAP in both plant recycling (up to 30%) and in-place recycling (up to 100%) [7,8]. In the Netherlands, 71% of the RAP is used in Hot Mixing Asphalt (HMA) and Warm Mixing Asphalt (WMA) [9]. However, using RAP materials in asphalt mixtures leads to durability concerns (e.g., increased moisture susceptibility and reduced cracking and fatigue resistance) due to aged and stiff bitumen binders in RAP materials [10,11]. On the other hand, aged bitumen in RAP materials can potentially improve the resistance of asphalt mixtures to permanent deformation [12,13].

Upon the addition of rejuvenators to aged bitumen, the thermo-mechanical and rheological properties of the binder could be restored, resulting in an improved service life of recycled asphalt pavements [14]. Rejuvenators have been successfully added to the asphalt mixtures containing RAP materials to reduce binder stiffness and provide the desired performance for longer service periods [15,16]. Rejuvenators with a high proportion of light components are added in aged bitumen to enhance their rheological and engineering properties. The use of rejuvenated binders in paving construction could provide many benefits such as reduced greenhouse gas emissions, reduced pressure on non-renewable natural resources, and reduced pollution from residue waste [17,18]. In the hot recycling method, soft bitumen and rejuvenators are usually used to restore the engineering properties of the aged binder. However, many problems with the rejuvenation of aged bitumen still exist. On the one hand, many kinds of rejuvenators have complex compositions and different rejuvenation effects, and the corresponding rejuvenation mechanism of these rejuvenators are still unclear [19]. On the other hand, the current evaluation methods of rejuvenated bitumen are incomplete and cannot estimate the rejuvenation effect accurately [20]. Table 1 shows various studies that adopted different chemical and rheological indices to evaluate the rejuvenation efficiency of variable rejuvenation conditions. In addition, the rejuvenation efficiency of rejuvenation cases strongly depends on different material factors, such as rejuvenator type/dosage and the aging degree of bitumen [21].

The rejuvenation efficiency using the G*-based parameters may depend on the testing frequency and temperature. However, many studies have selected only a few points from the master curves to assess the rejuvenation effectiveness of rejuvenators, and the restoration level of rheological performance across the entire temperature-frequency range [28,29]. To prevent any potential biases that may arise from arbitrary point selection within the frequency-temperature range, it is crucial to assess the rejuvenation effectiveness throughout the full-scale temperature-frequency spectrum.

Various micromechanics models are used to describe the complex modulus G* and phase angle δ master curves of bituminous materials, including the Maxwell model, Burgers model, standard linear solid model, and generalized Maxwell model [30]. Previous studies have shown that the 2S2P1D constitutive model can reflect well the viscoelastic behavior of fresh [31], aged [32], modified [33], and rejuvenated bitumen [34,35]. Additionally, the 2S2P1D model could describe the rheological behaviors of asphalt mastics [36], mortars [37], and mixtures [38,39] successfully. Furthermore, through detecting the variations in micromechanical properties of bituminous materials, the blending level between virgin and RAP-extracted binders [40] and the moisture susceptibility of asphalt mixtures [41] were also estimated.

This study aims to (i) investigate of the influence of rejuvenator type, dosage, and aging level on the rejuvenation efficiency of rheological and chemical properties of rejuvenated bitumen, (ii) explore the capability of viscoelastic models (namely 2S2P1D) on evaluating the rejuvenation efficiency, (iii) Discuss the relationship between chemistry and rheology of rejuvenated binders, and (iv) propose a set of chemo-rheological indicators for the evaluation of rejuvenation efficiency.

Fig. 1 illustrates a schematic of the research steps to achieve the paper objectives. Various factors affecting bitumen aging and rejuvenation, including rejuvenator type/dosage and bitumen aging level, will be investigated under different aging and rejuvenation conditions. Two parallel research lines will perform rheological tests and chemical characterizations. The first line will adopt viscoelastic models to describe the master curves of virgin, aged, and rejuvenated binders and examine the effects of rejuvenation conditions on the model's parameters and corresponding rejuvenation percentages. The second line will measure the chemical indices and relative rejuvenation effectiveness of various rejuvenated binders. The sensitivity of these models' parameters and chemical indices to all influence factors will be compared to propose critical indicators for developing evaluation criteria on rejuvenation efficiency. Lastly, the potential connections between the rheological constitutive models' parameters and chemical indices of all rejuvenated bitumen systems and their rejuvenation percentages will be explored and discussed.

2. Materials and methods

2.1. Materials

In this study, a 70/100 virgin bitumen and four different rejuvenators, namely bio-oil (BO), engine-oil (EO), naphthenic-oil (NO), and aromatic-oil (AO), were used. Table 2 lists the physical, chemical and mechanical properties of the studied bitumen and Table 3 shows the physio-chemical chemical characteristics of the rejuvenators.

2.2. Aging and rejuvenation of bitumen

Aged bitumen samples were manufactured using the Thin Film Oven (TFO) aging test at 163 °C followed by the Pressure Aging Vessel (PAV) at 100 °C. The aging time for short-term TFOT aging was 5 h, whereas the time for the long-term PAV test varied from 20h to 40h and 80h. In the following sections, the abbreviations VB, SAB, LAB20, LAB40, and LAB80 will be used for virgin bitumen, short-term aged bitumen, and long-term aged bitumen for 20, 40 and 60 h.

Next the rejuvenated binders were prepared by mixing the aged bitumen and rejuvenators at 160 °C for 10 min. The rejuvenator dosage was selected based on the aging level of the bitumen. For LAB20 aged bitumen, the contents of the rejuvenator are 1.25%, 2.5%, 3.75%, 5.0%, 7.5%, and 10%, while the rejuvenator dosage in both LAB40 and LAB80 binders

Table 1 – The commonly-used parameters for evaluating rejuvenation efficiency.

	Rejuvenator type	Rejuvenator dosage	Aging level	Evaluation index	Calculation formula	Ref
1	Commercial rejuvenator, Aromatic-oil, warm mix rejuvenator	10%, 7%, and 10%	RTFOT + PAV	Reversibility index R_M	$\frac{G_a^* - G_r^*}{G_a^* - G_u^*}$	[22]
2	FCC slurry, BUDGE, MDI	10%, 1%, and 3%	TFOT + PAV	Ductility index DI, softening point index SPI, and penetration index PI	$\frac{D_{rejuvenated}}{D_{fresh}}$ $\frac{SP_{rejuvenated}}{SP_{fresh}}$ $\frac{P_{rejuvenated}}{P_{fresh}}$	[23]
3	Tall oil, vegetal oil/ polymer, bio-oil, petroleum-based	5%	RAP-extracted (RA)	Softening index I_S	$\frac{\int_{-5}^{-1} \log G_{RA}^* df}{\int_{-5}^{-1} \log G^* df}$	[24]
4	Aromatic oil, light oil, vegetable oil	12%	TFOT 15h	Rejuvenation index RI	$\frac{(SI + CI)_{rejuvenated}}{(SI + CI)_{aged}}$	[25]
5	Tall oil, bio oils, aromatic extract, paraffinic oil, vegetable oils	9%, 8%, 8%, 10.5%, 13.5%, 8.5%, 11%	RTFO + PAV	Rejuvenation index RI	$\frac{\int_0^{40} E_{RAP}(x)dx \cdot \int_0^{40} WPTEnergy_{RAP}(x)dx}{\int_0^{40} E_{Rej}(x)dx \cdot \int_0^{40} WPTEnergy_{Rej}(x)dx}$	[26]
6	Epoxy soybean oil	6%	RTFO + PAV	Complex modulus regeneration index CMRI, phase angle regeneration index PARI	$\frac{G^*_{Rejuvenated\ asphalt}}{G^*_{SBSMA}}$, $\frac{\delta_{Rejuvenated\ asphalt}}{\delta_{SBSMA}}$	[27]

varies from 2.5% to 15% with an interval of 2.5%. The abbreviations BORB, EORB, NORB, and AORB were used to represent the bio-oil, engine-oil, naphthenic-oil, and aromatic-oil rejuvenated bitumen, respectively.

2.3. *Rheological and chemical characterizations*

The dynamic shear rheometer (DSR) and Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy were employed to assess the effects of rejuvenator type/ dosage and aging level of bitumen on the rejuvenation efficiency. Frequency sweep tests were performed on all bitumen samples using DSR with an increasing frequency of 0.1–100 rad/s. The testing temperature rises from 0 °C to 70 °C with an interval of 10 °C. The master curves of complex modulus (G*) and phase angle (δ) were constructed at a reference temperature of 20 °C.

At room temperature, functional groups of the virgin, aged, and rejuvenated bitumen were detected using an ATR-FTIR device in the wavenumber region of 600–4000 cm^{-1} using 12 scans. For each testing condition, three tests were implemented on each sample to ensure the reliability of the data.

3. Selection of micromechanical constitutive models

Several models have been used to fit the master curves of both complex modulus and phase angle of virgin and aged bitumen. In this study, the five different constitutive models (Fig. 2), namely Kelvin, Maxwell, Burgers, Generalized Maxwell, and 2 Spring-2 Parabolic-1 Dashpot (2S2P1D) models, are selected for describe the rheological behaviors of bituminous materials with variable aging and rejuvenation conditions.

The Kelvin and Maxwell models are described using Eqs (1) and (2):

$$\sigma = G\varepsilon + \eta\frac{d\varepsilon}{dt} \tag{1}$$

$$\frac{d\varepsilon}{dt} = \frac{1}{G}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} \tag{2}$$

where σ and ϵ are shear stress and strain; G represents the elastic modulus of the spring, and η refers to the viscosity of the dashpot.

The Burgers model is composed of the Kelvin and Maxwell models, which is defined as

$$\sigma + \left(\frac{\eta_1 G_1 + \eta_1 G_2 + \eta_2 G_1}{G_1 G_2}\right)\frac{d\sigma}{dt} + \frac{\eta_1\eta_2}{G_1 G_2}\frac{d^2\sigma}{dt^2} = \eta_1\frac{d\varepsilon}{dt} + \frac{\eta_1\eta_2}{G_2}\frac{d^2\varepsilon}{dt^2} \tag{3}$$

where G_1 and η_1 are the elastic modulus and viscosity parameters in the Maxwell element; Besides, the G_2 and η_2 are the elastic modulus and viscosity in the Kelvin element.

In addition, the Generalized Maxwell (GM) model consists of several Maxwell elements (shown in Fig. 2(d)), and the corresponding constitutive equation is listed below:

$$\sum_{k=0}^{n} P_k \frac{d^k\sigma}{dt^k} = \sum_{k=0}^{n} q_k \frac{d^k\varepsilon}{dt^k} \tag{4}$$

where p_k and q_k are material parameters. This study used a GM model with ten parallel Maxwell elements to fit master curves of the virgin, aged, and rejuvenated binders. Table 4 summarizes the mathematical equations of constitutive models fitting G* and δ master curves. The parameters of the

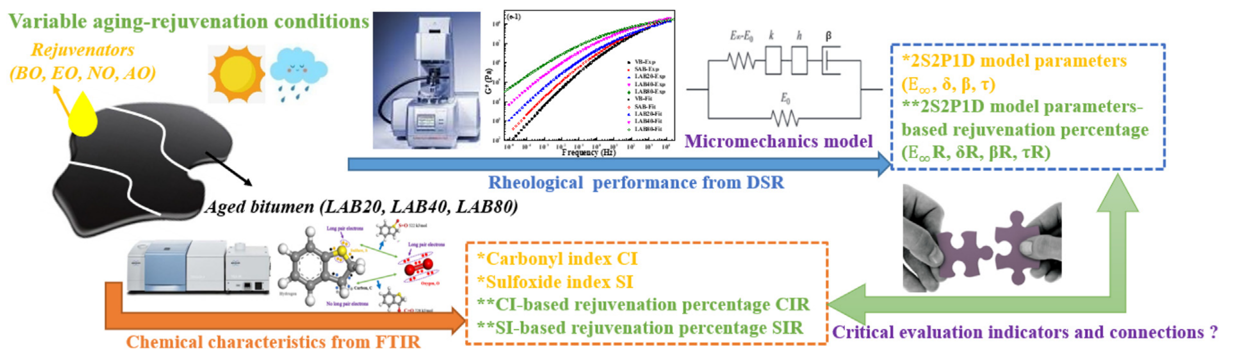

Fig. 1 – Research scheme of this paper.

constitutive models are determined by minimizing the mean relative error (MRE) as defined in Eq. (5).

$$\mathrm{MRE} = \sum \frac{\left|G_f^* - G_t^*\right|}{G_t^*} + \sum \frac{\left|\delta_f - \delta_t\right|}{\delta_t} \tag{5}$$

where G_f^* and G_t^* are the fitting and testing values of complex modulus, and δ_f and δ_t are the phase angle parameters from the constitutive models and experiments.

Currently, the 2S2P1D model was developed, composed of 2 spring components, 2 parabolic elements, and 1 dashpot element (displayed in Fig. 2(e)), to effectively predicts the linear viscoelastic (LVE) properties of bituminous materials. The analytical expression of the complex modulus of the 2S2P1D model is shown in Eq. (6).

$$G^*(i\omega) = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}} \tag{6}$$

where E_0 and E_∞ denote the static modulus and glassy modulus of bituminous materials; k and h parameters represent the dimensionless exponents of two parabolic components ($1 > h > k > 0$); δ is a positive constant, and τ parameter refers to the temperature-dependent characteristic time; β is a dimensionless constant associated with a Newtonian viscosity parameter η:

$$\beta = \frac{\eta}{(E_\infty - E_0)\tau} \tag{7}$$

Based on Euler's equation, the terms of $(i\omega\tau)^{-k}$ and $(i\omega\tau)^{-h}$ in Eq. (6) can be expanded as:

$$(i\omega\tau)^{-k} = |\omega\tau|^{-k}\left[\cos\left(\frac{k\pi}{2}\right) - i\,\mathrm{sgn}(\omega\tau)\sin\left(\frac{k\pi}{2}\right)\right] \tag{8}$$

$$(i\omega\tau)^{-h} = |\omega\tau|^{-h}\left[\cos\left(\frac{h\pi}{2}\right) - i\,\mathrm{sgn}(\omega\tau)\sin\left(\frac{h\pi}{2}\right)\right] \tag{9}$$

In addition, the 2S2P1D model for phase angle (δ) master curves is expressed below:

$$\delta = \arctan\frac{\delta|\omega\tau|^{-k}\mathrm{sgn}(\omega\tau)\sin\left(\frac{k\pi}{2}\right) + |\omega\tau|^{-h}\mathrm{sgn}(\omega\tau)\sin\left(\frac{h\pi}{2}\right) + (\omega\tau\beta)^{-1}}{1 + \delta|\omega\tau|^{-k}\cos\left(\frac{k\pi}{2}\right) + |\omega\tau|^{-h}\cos\left(\frac{h\pi}{2}\right)} \tag{10}$$

4. Results and discussion

4.1. *Micromechanical modelling on G* and δ master curves*

Fig. 3 illustrates the results of the G* and δ master curves constructed using the different micromechanical constitutive models. The minimization procedure was set up in Excel. The parameters for the different models are summarized in Table S1-S5 in the supplementary material section. The values of G* for bitumen exhibit a significant increase, while the

Table 2 – The basic properties of virgin bitumen.

Items	Properties	Value	Test standard
Physical indicators	Density (25 °C, g/cm^3)	1.017	EN 15326 [42]
	Penetration (25 °C, 1/10 mm)	91	ASTM D35 [43]
	Softening point (°C)	48.0	ASTM D36 [44]
	Viscosity (135 °C, Pa·s)	0.80	AASHTO T316 [45]
	Carbon C (wt%)	84.06	
	Hydrogen H (wt%)	10.91	
Element analysis	Nitrogen N (wt%)	0.90	ASTM D7343 [46]
	Oxygen O (wt%)	0.62	
	Sulfur S (wt%)	3.52	
	Asphaltene As (wt%)	12.8	
SARA fractions	Resin R (wt%)	30.3	ASTM D4124 [47]
	Aromatic A (%)	53.3	
	Saturate S (%)	3.6	
Mechanical properties (60 °C, 1.6 Hz)	Complex modulus G* (kPa)	2.4	AASHTO M320 [48]
	Phase angle δ (°)	84.5	

Table 3 – The physical and chemical indicators of four rejuvenators.

Items	Rejuvenators	BO	EO	NO	AO
Physical	Density (25 °C, g/cm^3)	0.911	0.833	0.875	0.994
	Viscosity (25 °C, cP)	50	60	130	63,100
	Flash point (°C)	265–305	>225	>230	>210
Chemical	Nitrogen N (%)	0.15	0.23	0.12	0.55
	Carbon C (%)	76.47	85.16	86.24	88.01
	Hydrogen H (%)	11.96	14.36	13.62	10.56
	Sulfur S (%)	0.06	0.13	0.10	0.48
	Oxygen O (%)	11.36	0.12	0.10	0.40
	Mn (g/mol)	286.43	316.48	357.06	409.99

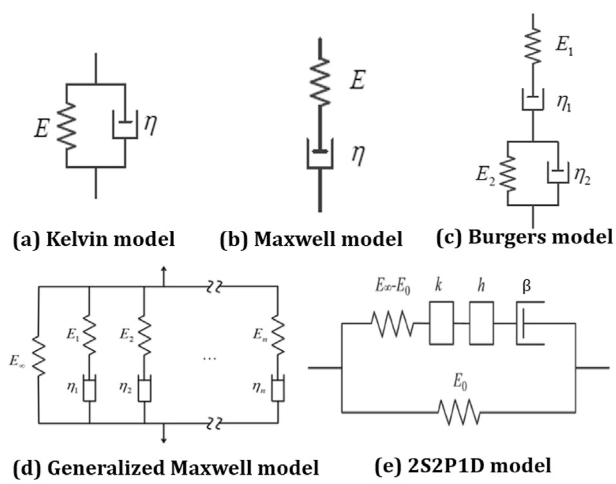

Fig. 2 – Schematic representations of constitutive models for bituminous materials.

δ parameter displays a reduction trend as the aging time is extended. This suggests that the bitumen undergoes a transformation into a stiffer and more elastic material during the aging process. In terms of modelling effectiveness, it can be observed that the fitting curves on G* master curves for both virgin and aged binders using the Burgers model closely align with the experimental data. However, there exists a significant difference between the fitting and experimental results in terms of δ values. The Kelvin and Maxwell models show poor fitting efficiency on both G* and δ master curves. Conversely, the utilization of the Generalized Maxwell model effectively fits the master curves, whereas the fitting efficiency depends on the number of parallel parts in the entire model. Despite the success of the Generalized Maxwell model, there remains a noticeable discrepancy between the shape of the δ master curves obtained through experiments and modelling.

The fitting results on 2S2P1D model of G* and δ master curves of bitumen are shown in Figs. 3 (e–1) and (e–2). The 2S2P1D model exhibits the best fitting efficacy for both G* and δ master curves of all virgin and aged binders. However, there exists a minor discrepancy in δ values between tests and models when the frequency is below 10^{-4} Hz. The long-term aging remarkably influences E_∞, δ_1, β, and τ_2 parameters in the 2S2P1D models. In the following sections, the impacts of different rejuvenation conditions on the G* and δ master curves will be investigated using these sensitive parameters

4.2. *Influence of long-term aging on sensitive parameters in 2S2P1D models*

Understanding the micromechanical models' characteristics of bitumen under variable long-term aging conditions is crucial before investigating rejuvenation. Fig. 4 presents a summary of the 2S2P1D model parameters of various virgin and aged binders, along with the correlation equations. As long-term aging prolongs, the E_∞ and δ parameters of bitumen exhibit a decreasing trend, while both β and τ values gradually increase. Linear relationships exist between the long-term aging time and the E_∞ and τ parameters of bitumen. Based on the absolute values of equation slopes, the τ parameter is more sensitive to long-term aging time than the E_∞ parameter.

Table 4 – The mathematical expressions on the G* and δ master curves [49].

Constitutive models	Master curves of G*(i ω)	Master curves of δ(i ω)
Kelvin	$G + i\eta\omega$	$\arctan\frac{G}{\omega\eta}$
Maxwell	$\frac{G\omega^2\eta^2 + iG^2\omega\eta}{E^2+\omega^2\eta^2}$	$\arctan\frac{\omega\eta}{G}$
Burgers	$\frac{1}{\left(\frac{1}{G_1}+\frac{G_2}{G_2^2+\eta_2^2\omega^2}\right)-\left(\frac{1}{\eta_1\omega}+\frac{\eta_2\omega}{G_2^2+\eta_2^2\omega^2}\right)i}$	$\arctan\frac{\left(\frac{1}{\eta_1\omega}+\frac{\eta_2\omega}{G_2^2+\eta_2^2\omega^2}\right)}{\left(\frac{1}{G_1}+\frac{G_2}{G_2^2+\eta_2^2\omega^2}\right)}$
Generalized Maxwell	$\sum_{k=1}^{n}\frac{G_k\omega^2\eta_k^2+iG_k^2\omega\eta_k}{G_k^2+\omega^2\eta_k^2}$	$\sum_{k=1}^{n}\frac{G_k}{\omega\eta_k}$

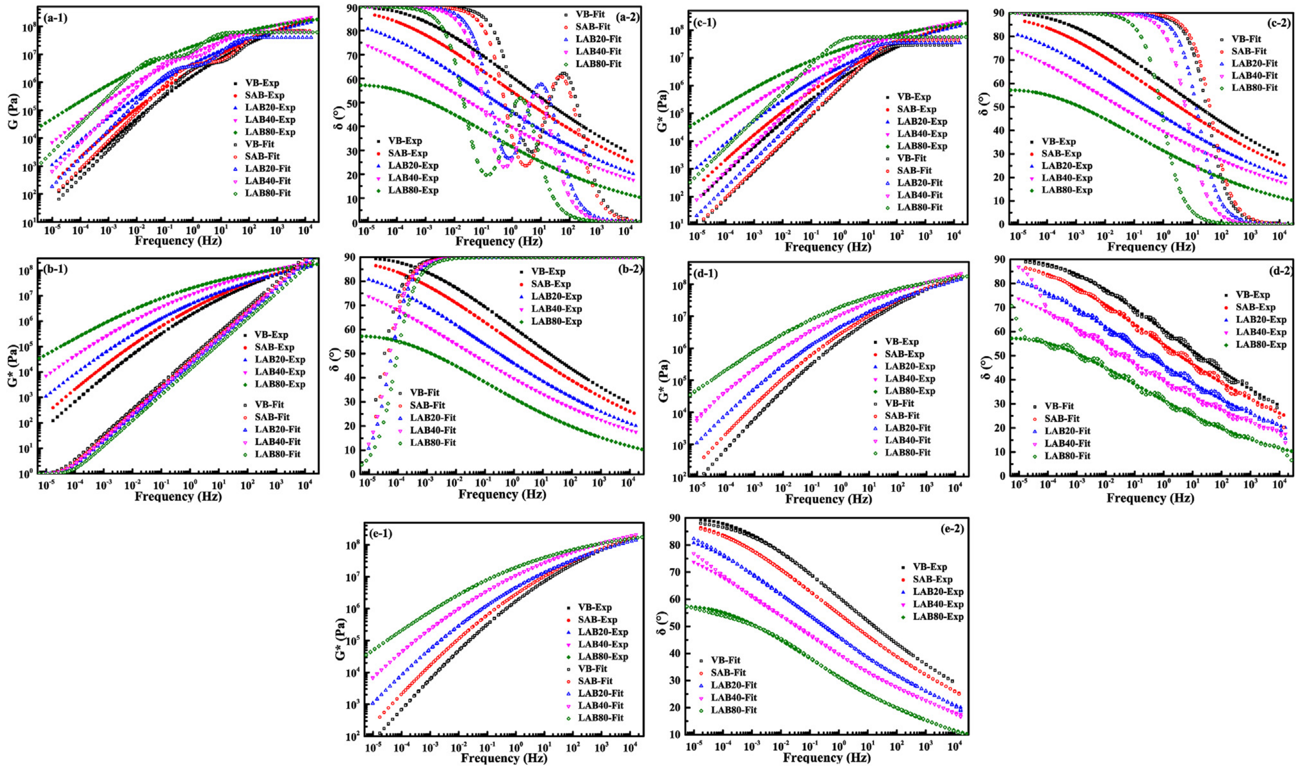

Fig. 3 — Mater curves of G* and δ of virgin and aged bitumen using the (a) Burgers, (b) Kelvin, (c) Maxwell, (d) Generalized Maxwell, and (e) 2S2P1D micromechanical models.

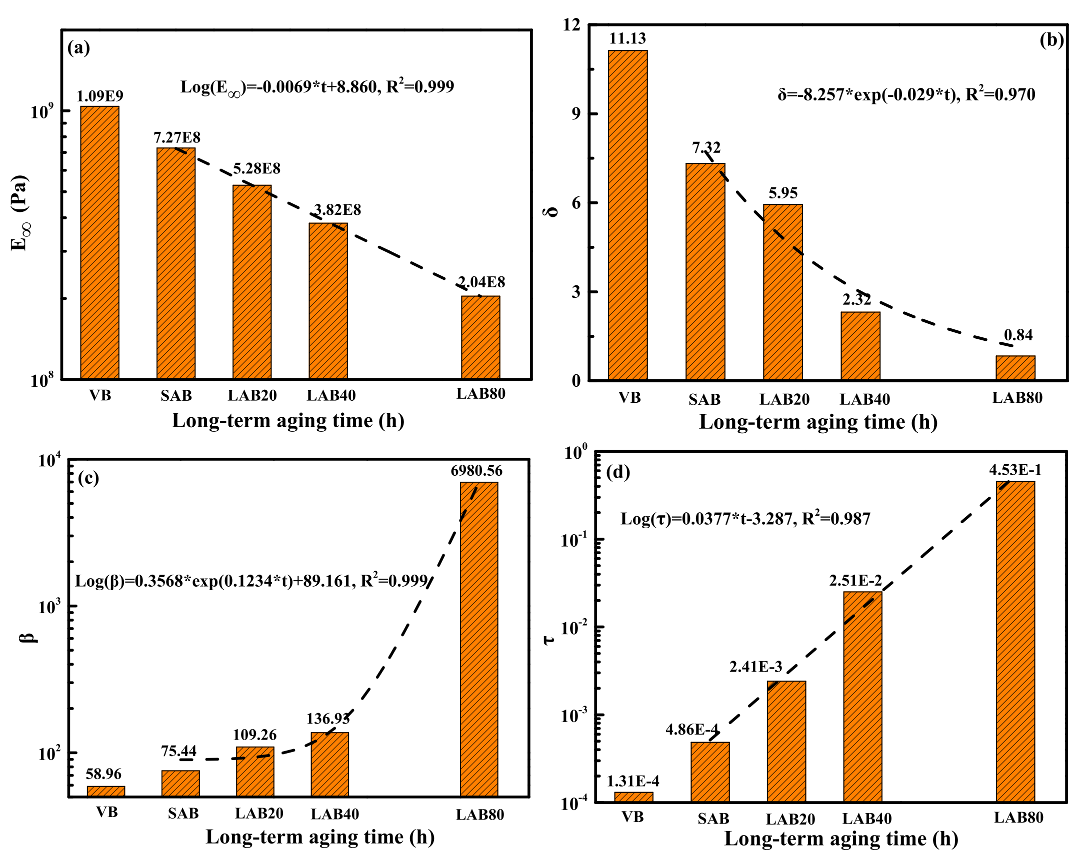

Fig. 4 — The 2S2P1D model parameters of virgin and aged bitumen.

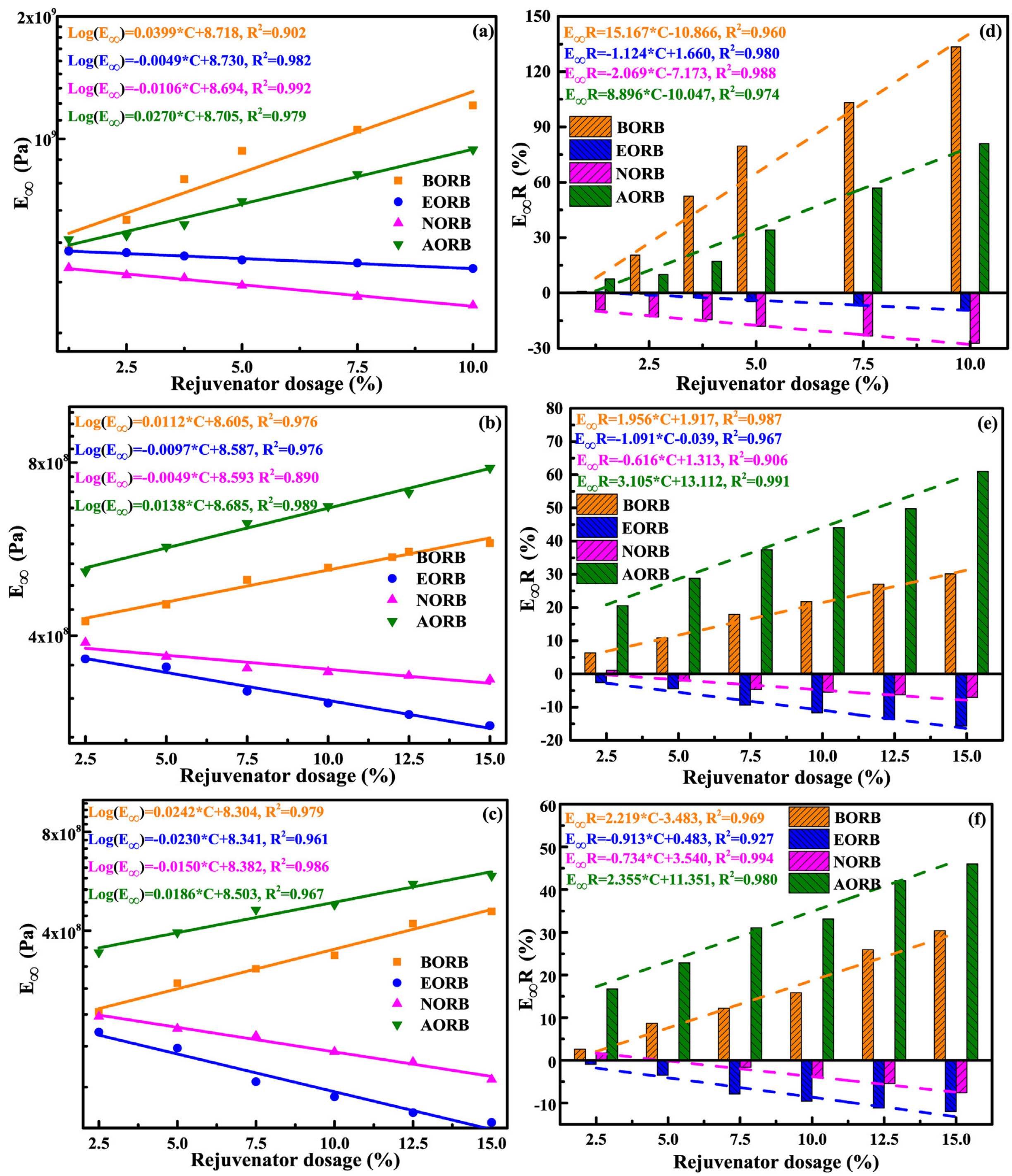

Fig. 5 – Effects of rejuvenation on E_∞ (a–c) and $E_\infty R$ (d–f) of aged bitumen.

On the other hand, both δ and β parameters show exponential changes with the increase in long-term aging time. It is worth noting that there is a sudden enlargement in the β parameter from 136.93 to 6980.56 when the long-term aging time increases from 40h to 80h. The observation may be attributed to the limited sensitive region of the β parameter to long-term aging time, rendering it ineffective when the aging level exceeds 40h. This point will be further addressed and discussed in the rejuvenation section below.

4.3. *Sensitivity study of rejuvenation on the 2S2P1D model parameters*

The efficacy of various rejuvenators in restoring the characteristics of aged bitumen is quantitatively evaluated through rejuvenation percentages based on the restoration level of these 2S2P1D model parameters. The rejuvenation percentage (XR) is calculated using Eq. (11).

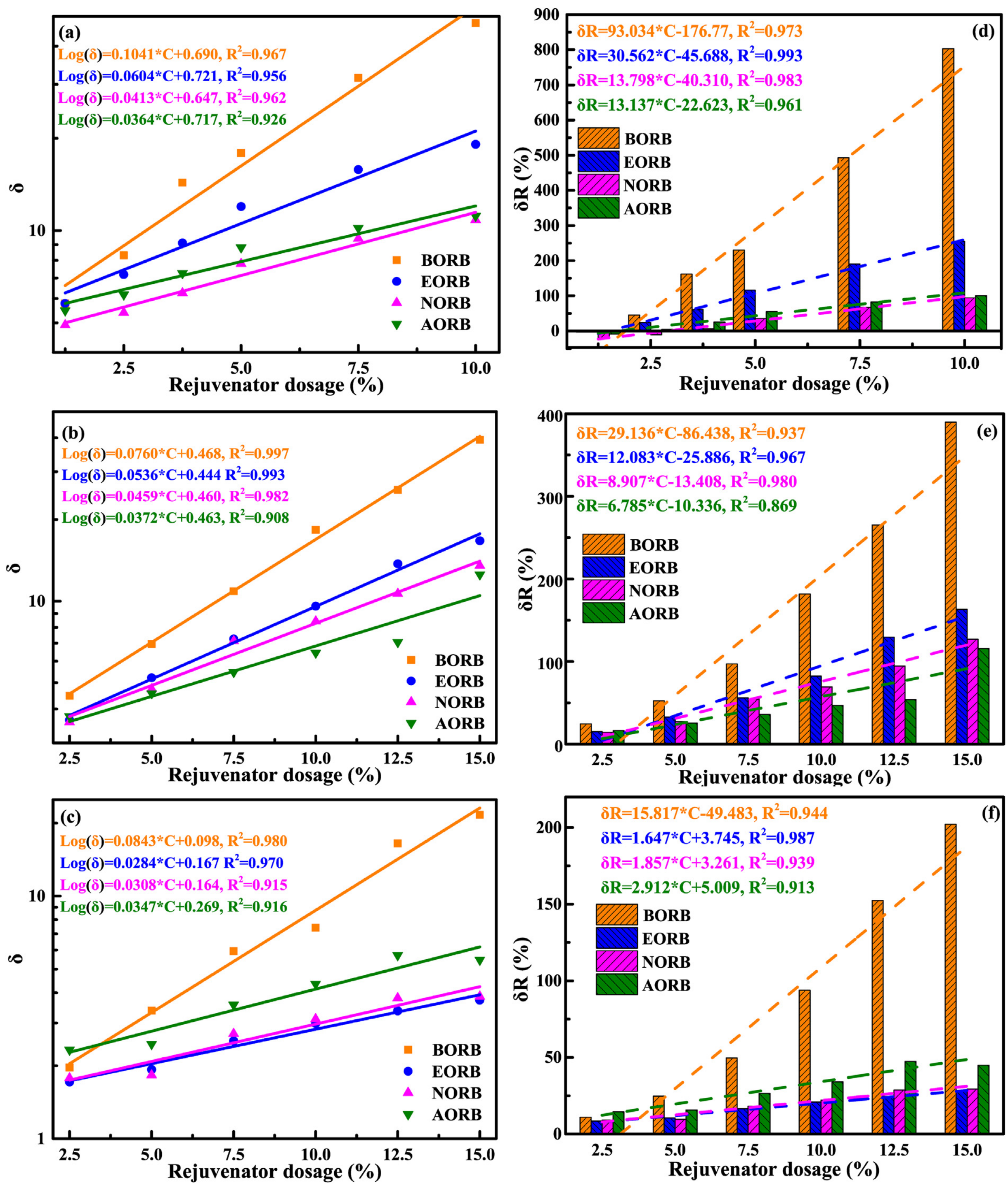

Fig. 6 – Effects of rejuvenation on δ (a–c) and δR (d–f) of aged bitumen.

$$XR = \frac{X_{aged} - X_{rejuvenated}}{X_{aged} - X_{virgin}} * 100 \tag{11}$$

where X represents one of the 2S2P1D model parameters (E_∞, δ, β, or τ); X_{aged}, $X_{rejuvenated}$, and X_{virgin} denote the model parameter value of aged, rejuvenated, and virgin bitumen, respectively. A positive rejuvenation effect of the rejuvenator on the 2S2P1D model parameter of aged bitumen to the virgin binder is indicated by an XR value greater than 0.

4.3.1. *The E_∞ and E_∞ R parameters*

The E_∞ and E_∞R values of rejuvenated bitumen with variable rejuvenator types, dosages, and aging levels are illustrated in Fig. 5. Rejuvenator dosage has a linear correlation with $\text{Log}(E_\infty)$ values regardless of rejuvenator type. When the rejuvenator dosage and aging level of bitumen are fixed, bio-oil and aromatic-oil rejuvenated binders have higher E_∞ values than engine-oil and naphthenic-oil rejuvenated binders. However,

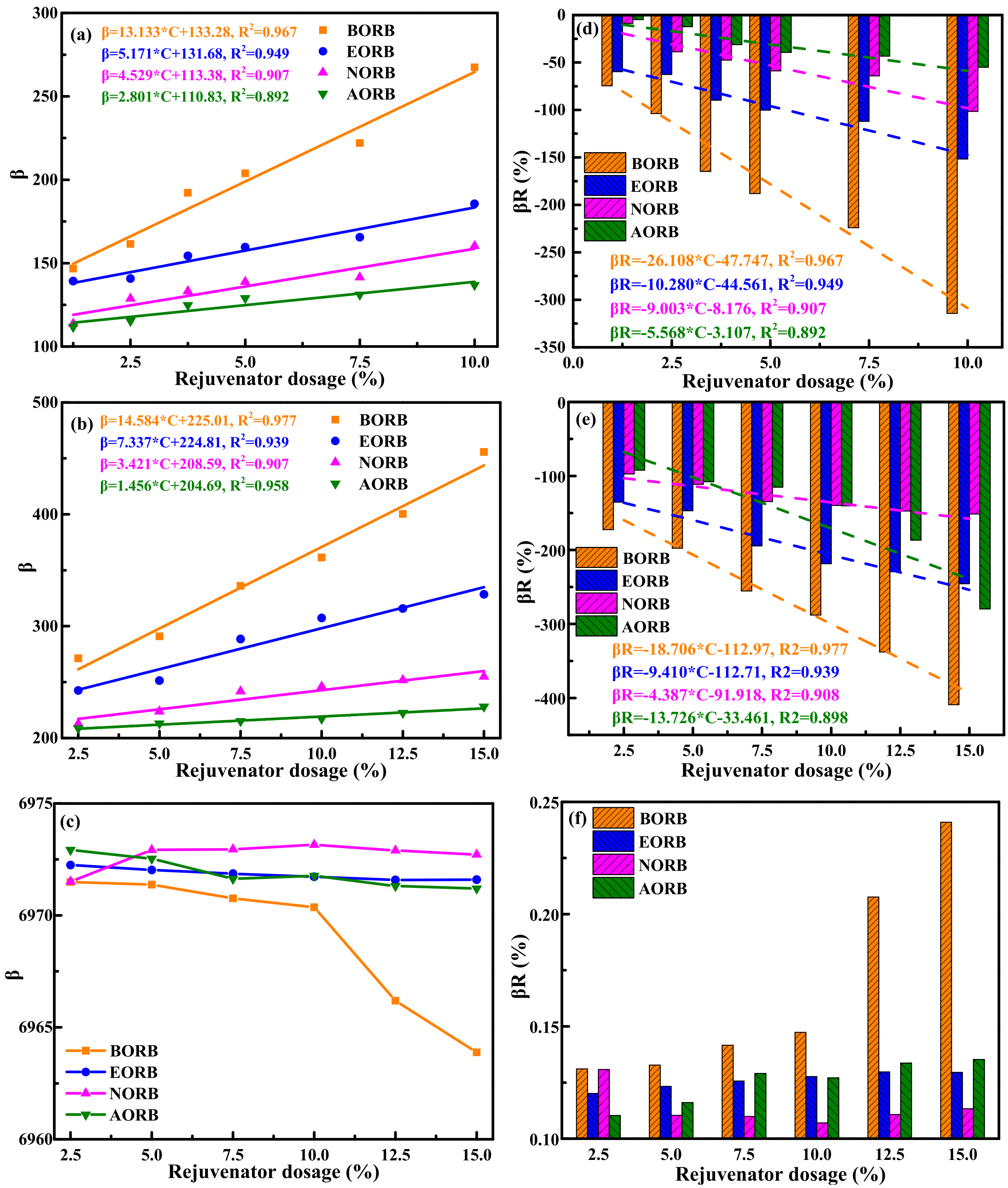

Fig. 7 – Effects of rejuvenation on β (a–c) and βR (d–f) of aged bitumen.

the order of E_∞ values between BORB/AORB or EORB/NORB depends on the bitumen's aging level. Rejuvenator type strongly affects the influence of rejuvenator dosage on E_∞ parameter of rejuvenated bitumen. The E_∞ values of bio-oil and aromatic-oil rejuvenated binders can be restored linearly, while engine-oil and naphthenic-oil fail to achieve the rejuvenation goal. The $E_\infty R$ values of rejuvenated binders depend on the aging grade of bitumen. The BO rejuvenator exhibits a higher $E_\infty R$ than AO in the LAB20 binder, whole AO shows a stronger rejuvenation capacity than BO in both LAB40 and LAB80 aged bitumen. The $E_\infty R$ values of BO and AO rejuvenated binders are more sensitive to rejuvenator dosage variation than the EO and NO rejuvenated binders. Lastly, the obtained correlation equations can predict the E_∞ parameters in the 2S2P1D models of rejuvenated bitumen with other rejuvenator contents without any repeated experiment.

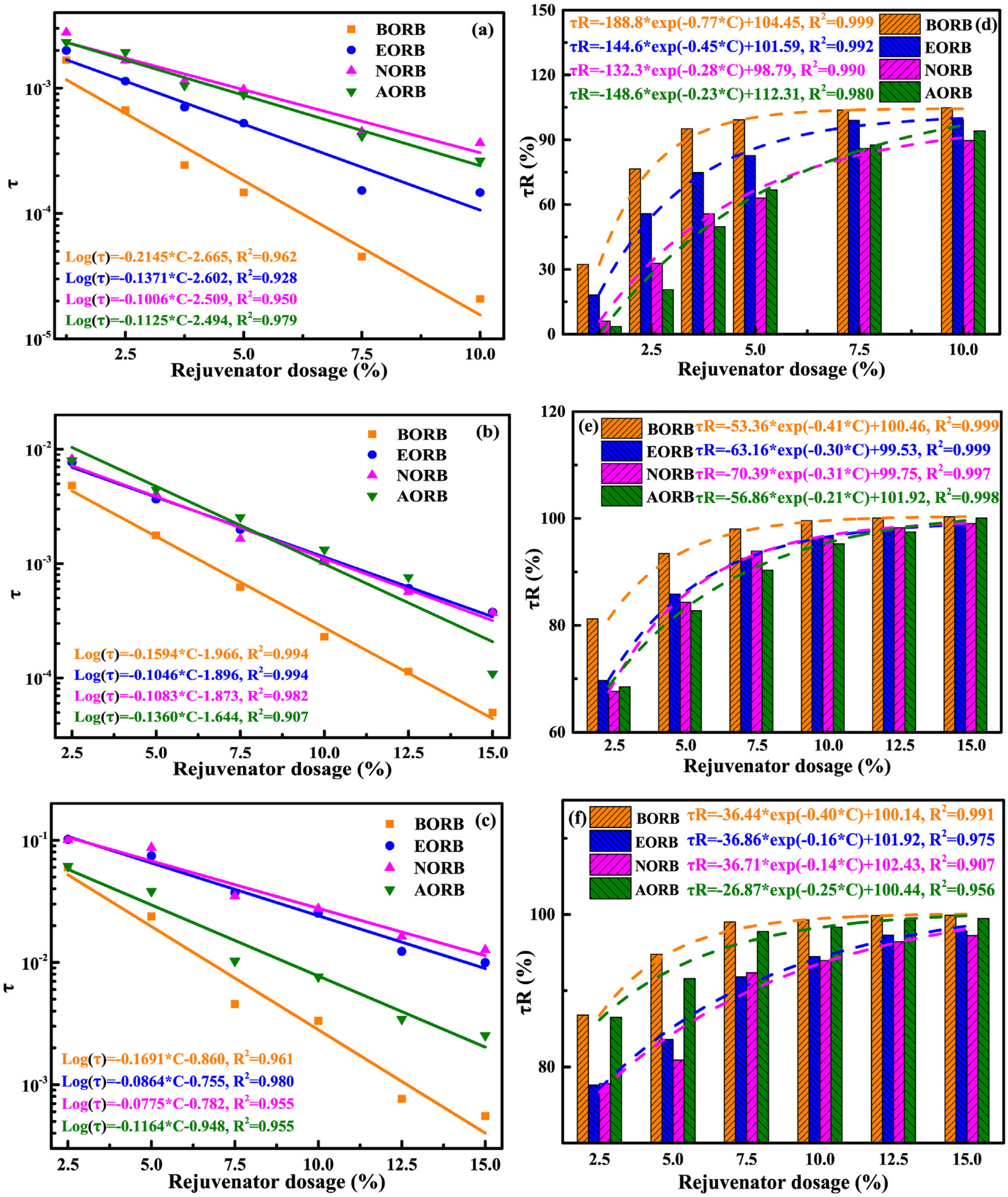

Fig. 8 – Effects of rejuvenation on τ (a–c) and τR (d–f) of aged bitumen.

4.3.2. *The δ and δR parameters*

The influence of rejuvenator dosage on the δ parameters in the 2S2P1D models of aged bitumen LAB20, LAB40, and LAB80 are displayed in Fig. 6 (a)-(c), respectively. It is observed that all rejuvenators show positive effects on the δ parameter, which decreases significantly with the increase of aging level. It indicates that the rejuvenator's involvement can restore the aged bitumen's δ parameter towards the virgin binder level. The bio-oil rejuvenated bitumen exhibits the largest δ value regardless of the rejuvenator dosage and aging grade of bitumen. As the increase of rejuvenator dosage, the δ parameter of all rejuvenated bitumen shows a linearly enlarging trend. Moreover, the order for the sensitivity of δ parameter to rejuvenator dosage of different rejuvenated binders is BORB > EORB > NORB > AORB, which of the latter three are very close in the LAB80 case.

The results of δR parameters of various rejuvenated binders are shown in Fig. 6 (d)−(f). It is worth mentioning that the δR values of all rejuvenated bitumen are positive, implying that all rejuvenators selected in this study show affirmative functions in restoring the δ parameter of aged bitumen. Therefore, the δ parameter is more effective in assessing the rejuvenation efficiency of all rejuvenators than the E_∞ parameter, which only can reflect the rejuvenation work of bio-oil and aromatic-oil rejuvenators. The δR parameter of rejuvenated bitumen enlarges linearly as the rejuvenator dosage rises. Nevertheless, the δR values of different rejuvenated bitumen change significantly, and the bio-oil rejuvenated bitumen shows a maximum δR regardless of rejuvenator dosage and aging degree. Additionally, the aging level of bitumen affects the δR values of rejuvenated bitumen, especially for the order for δR of engine-oil, naphthenic-oil, and aromatic-oil rejuvenated binders. When the aging level of bitumen is not high (LAB20), the δR values of EO rejuvenated bitumen are higher than the NO and AO rejuvenated binders. With the aging level deepening, the δR values of rejuvenated bitumen are weakened, which agrees well with the rejuvenation efficiency based on rheo-mechanical performance [50]. When the aged bitumen is LAB40, the magnitude for the δR parameter is EO > NO > AO, which reverses totally when the aging level of bitumen rises to LAB80. Overall, the parameter δ of the 2S2P1D model is an effective indicator in estimating the rejuvenation efficiency of various rejuvenators in aged binders.

4.3.3. *The β and βR parameters*

The β and βR results of all rejuvenated binders with variable rejuvenator type/dosage and aging level of bitumen are demonstrated in Fig. 7. With the rejuvenator dosage increasing, the β parameters of rejuvenated binders with LAB20 and LAB40 aged bitumen enlarge linearly. The β parameter loses its sensitivity to evaluate the effects of rejuvenator type/dosage on the rejuvenation efficiency when the aging level of bitumen is severe (LAB80). A similar phenomenon was observed for the aging evaluation of bitumen with the β parameter. For both LAB20 and LAB40 cases, there is a significant difference in β values between rejuvenated bitumen with different rejuvenator types and dosages. In addition, the magnitude of β value and its sensitivity to rejuvenator dosage of various rejuvenated binders with aging grades of LAB20 and LAB40 is the same as BORB > EORB > NORB > AORB. Therefore, the β parameter seems suitable for significantly evaluating and distinguishing rejuvenator type and dosage effects in LAB20 and LAB40 aged binders.

Nevertheless, the β values of all rejuvenated bitumen are larger than that of corresponding aged bitumen, resulting in the βR parameter's negative values. It indicates that the addition of rejuvenators cannot restore the β value in the 2S2P1D model of aged bitumen, and the β parameter fails to play a role in assessing the rejuvenation efficiency of these rejuvenators on aged bitumen, which is expected to be similar to the restoration of rheological and mechanical performance. Furthermore, the βR parameters of LAB20 and LAB40 rejuvenated binders are correlated linearly with the rejuvenator dosage, which is not observed in the LAB80 case. Based on these restrictions, the β parameter is excluded from the appropriate indicators for rejuvenation efficiency evaluation of different rejuvenators in aged binders.

4.3.4. *Parameter τ and relative rejuvenation percentage τR*

The τ and τR values of different rejuvenated binders are presented in Fig. 8. It is worthwhile mentioning that the adjunction of rejuvenators would reduce the τ values, which show a linear decreasing trend as the increment of rejuvenator dosage regardless of rejuvenator type and aging grade of bitumen. It is converse to the effect of long-term aging time on increasing τ parameter of bitumen, which was demonstrated in Fig. 4(d). For all aged bitumen and rejuvenator dosage cases, the τ values of bio-oil rejuvenated bitumen are the lowest, which denotes that the bio-oil rejuvenator exhibits a stronger capacity for restoring the τ parameter of aged bitumen than the other three rejuvenators. However, the aging grade of bitumen strongly affects the order for τ values of bio-oil, engine-oil, and aromatic-oil rejuvenated binders. When the aged bitumen is LAB20, the τ values of EORB are lower than NORB and AORB. However, these three rejuvenated binders exhibit similar τ values in the LAB40 binder, while the AORB shows a lower τ parameter in LAB80. It is noticed that the τ values of EORB and NORB specimens almost coincide in LAB40 and LAB80 binders, indicating that it is difficult to use the τ parameter to distinguish the difference in rejuvenation efficiency of engine-oil and naphthenic-oil rejuvenators. Furthermore, the τ values of the BORB binder exhibit the largest sensitivity level to the variation of rejuvenator dosage, followed by AORB and EORB, while the impact of naphthenic-oil rejuvenator on the τ parameter is the faintest.

The τ-based rejuvenation percentage τR values of various rejuvenated binders are calculated and shown in Fig. 8 (d)−(f). The positive τR values reveal that all rejuvenators can somewhat recover the τ index of aged bitumen. Interestingly, the τR parameters of all rejuvenated bitumen present an exponential growth trend as the increase of rejuvenator dosage, which eventually converges at 100%. It manifests that the impact of rejuvenator content on the rejuvenation percentage of τ values gradually becomes lower. In other words, the τ parameter is not sensitive to a high concentration of rejuvenators. The bio-oil rejuvenator exhibits the strongest capacity to restore the τ value of aged bitumen to the virgin bitumen level. However, the difference in restoration level on the τ parameter between the other three rejuvenators varies with the aging grade of bitumen. When the aging level is slight (LAB20), the engine-oil has a higher τR value than the aromatic-oil rejuvenator. At the same time, the latter presents a greater recoverable efficiency on the τ parameter than the former as the aging level deepens. It is concluded that the τ parameter is available to be as an effective evaluation indicator for rejuvenation efficiency, but it will be invalid for assessing the influence of rejuvenator dosage on rejuvenation percentage when the rejuvenator content exceeds one point.

4.4. *Influence of long-term aging on carbonyl index and sulfoxide index of bitumen*

It is generally recognized that the rheological behaviors of bituminous materials are strongly associated with the

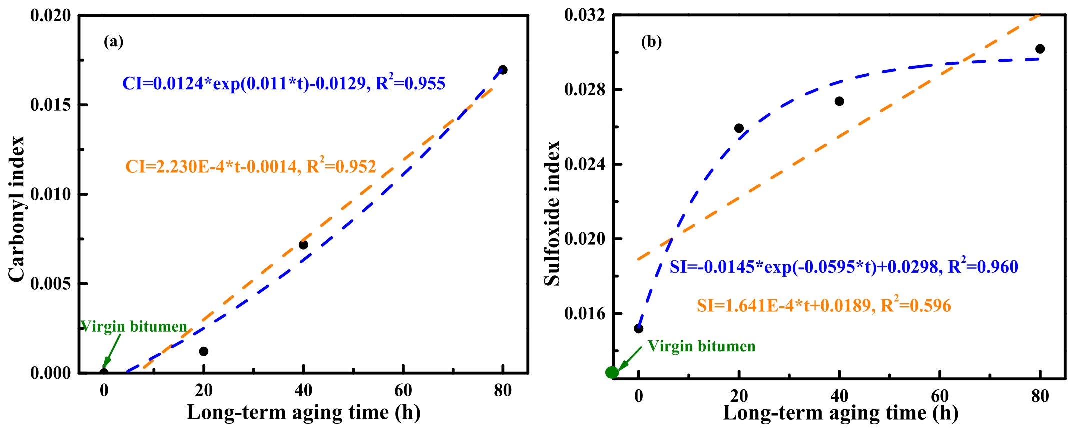

Fig. 9 – The CI and SI parameters of virgin and aged bitumen.

internal chemical characteristics, such as the ratio of saturate (S), aromatic (A), resin (R), and asphaltene (As) fractions, functional groups distribution, etc. In this study, the effects of aging and rejuvenation on both the carbonyl index (CI) and sulfoxide index (SI) of bitumen with changeable rejuvenator types and aging grades are investigated to check whether they are effective chemical indicators to evaluate the rejuvenation efficiency of various rejuvenators in several rejuvenator dosage/aging level conditions. Meanwhile, the potential connections between chemical indices and rheological parameters from the 2S2P1D micromechanics models and their derived rejuvenation percentages will be explored.

4.4.1. *CI and SI variations of bitumen during long-term aging*

Fig. 9 displays bitumen's CI and SI parameters versus long-term aging time. Both CI and SI values exhibit significant increasing trends as the aging time prolongs. It is due to the formation of C=O and S=O groups in bitumen molecules during the oxidation reactions under thermo-oxygen conditions. However, the variation law of CI and SI parameters are significantly different. To better compare, linear and exponential fitting equations are applied to find correlations between long-term aging time with CI and SI parameters. After reviewing the R^2 values of correlation equations, it is found that the CI value shows a linearly growing trend as the increase of aging time, while the SI parameter of bitumen enlarges exponentially with a convergence point. The difference in CI and SI variation trends is due to the different amounts of reactive carbon and sulfur atoms. The number of sulfur atoms in bitumen molecules is limited, which are almost reacted with oxygen completed with a long aging time. It should be mentioned that the measurement of CI and SI values of aged bitumen is a starting point to explore the rejuvenation efficiency of various rejuvenators. The obtained correlations formulas can help researchers predict the initial CI and SI values of aged bitumen with changeable long-term aging time without cumbersome experiments. Meanwhile, the aging state of one RAP binder can be estimated with measured chemical indices and their determinate relationships with aging time.

4.4.2. *Parameter CI and relative rejuvenation percentage CIR*

The combined effects of rejuvenator dosage/type and aging degree of bitumen on the carbonyl index of rejuvenated binders are reflected in Fig. 10. It can be seen that the addition of all rejuvenators reduces the CI value of aged bitumen, and the CI parameters of rejuvenated binders show a linear increasing law as the rejuvenator dosage rises. Meanwhile, the rejuvenator type and aging grade of bitumen significantly affect the CI values of rejuvenated bitumen. Interestingly, the CI values of bio-oil rejuvenated bitumen are lower than others, indicating that the bio-oil rejuvenator shows the greatest restoration effect of the CI parameter of an aged binder. A high aging level of bitumen is expected to result in a large CI value of rejuvenated bitumen. The major difference in CI values of rejuvenated binders with LAB20, LAB40, and LAB80 demonstrates that the influence of aging grade is much more significant than the rejuvenator type and dosage. In addition, the dependence of CI values on the rejuvenator dosage of various rejuvenated binders also relies on the rejuvenator type and aging degree. Based on the absolute slope values, the CI values of bio-oil rejuvenated bitumen exhibit the largest sensitivity to rejuvenator content, followed by the AORB, NORB, and EORB binders. Apart from the comparison, it is important to mention that it is possible to predict the CI values of rejuvenated bitumen with other rejuvenator contents.

Similar to constitutive modes' parameters, the rejuvenation efficiency of different rejuvenators on the chemical indices of aged bitumen is estimated by the rejuvenation percentage, which is calculated as follows:

$$YR = \frac{Y_{aged} - Y_{rejuvenated}}{Y_{aged} - Y_{virgin}} * 100 \quad (12)$$

where YR represents the chemical index Y-based rejuvenation percentage, and Y can be carbonyl index (CI) or sulfoxide index (SI); Y_{aged}, $Y_{rejuvenated}$, and Y_{virgin} denote the chemical index of aged, rejuvenated, and virgin bitumen, respectively.

The curves of CI-based rejuvenation percentage CIR of various rejuvenated bitumen as a function of rejuvenator concentration are drawn in Fig. 11. The CIR values of all rejuvenated binders are positive and lower than 100%,

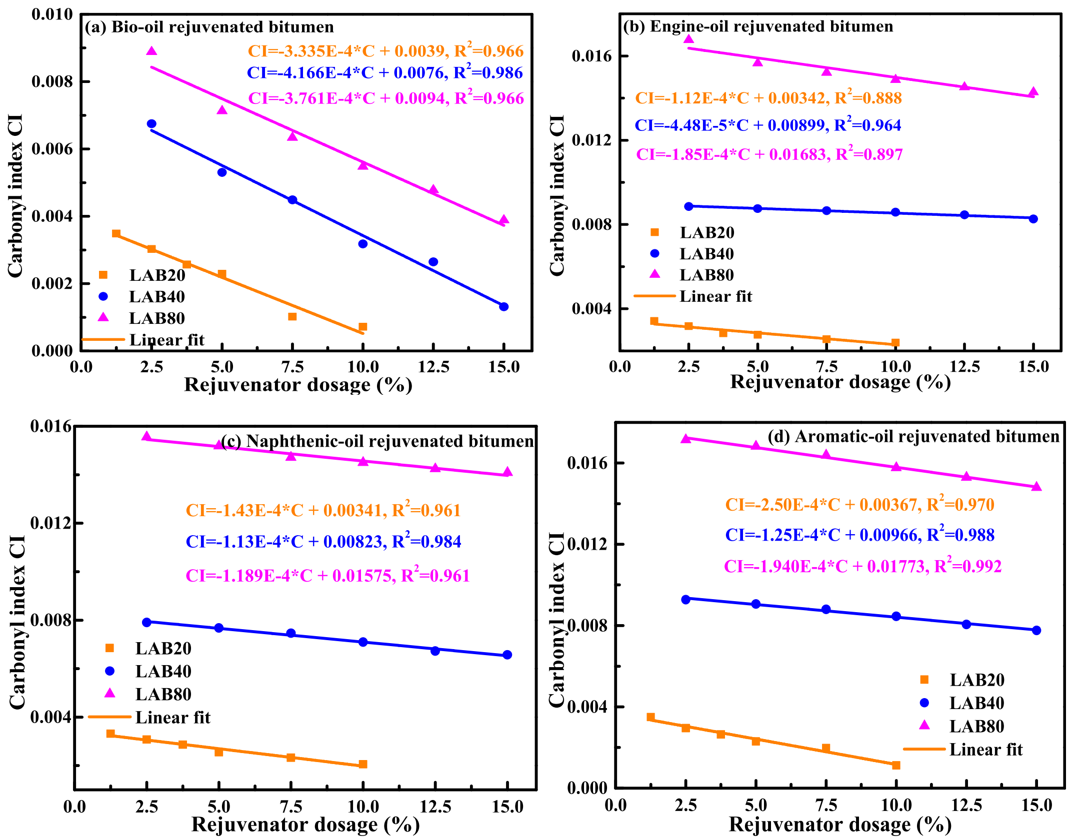

Fig. 10 – Variations of CI parameter of rejuvenated bitumen versus rejuvenator dosage.

showing that the rejuvenation conditions selected in this study fail to fully recover the CI value of aged bitumen to the virgin bitumen point. The CIR values of all rejuvenated binders present a linear intensifying tendency as the rejuvenator content enlarges. The underlying mechanism is mainly because the fusion of functional groups in rejuvenators would dilute the CI concentration of the whole rejuvenated bitumen. Regardless of rejuvenator dosage and aging level, the CIR values of bio-oil rejuvenated bitumen is the highest, and thus the bio-oil presents the greatest rejuvenation efficiency on the CI parameter of the aged binder. Additionally, the sensitivity of the CIR parameter to the enlarged rejuvenator dosage of BORB binder is the largest.

Compared to the EORB, the involvement of the naphthenic-oil rejuvenator shows a more significant effect on lessening the CI parameter of aged bitumen. From the Gas chromatography-mass spectrometry (GC-MS) results (see Fig. 12 [51]), it can be found that the bio-oil rejuvenator is mainly composed of various unsaturated fatty acid molecules, and the ester groups inside present a strong FTIR peck at 1750 cm^{-1}, which is separated from C=O peak (1650-1720 cm^{-1}) during the calculation of CIR values of BORB binder. Meanwhile, oxygen-containing functional groups in EO, NO, and AO rejuvenators would slow down the reduction rate of CI parameter in aged bitumen. Interestingly, the impact of aromatic-oil on the CIR values of AORB binder strongly depends on the aging level of bitumen. As the aging degree of bitumen deepens, the position of AORB in sorting CIR parameters is gradually lower.

Nevertheless, the slope values of AORB in the correlation formulas are larger than that of EORB and NORB. It suggests that the influence of rejuvenator concentration on the CIR values of AORB is more obvious than the EORB and NORB binder. However, the complex mechanism of the difference in CI and CIR values of various rejuvenated binders should be further studied. In general, the CI parameter can be used to distinguish the rejuvenation efficiency of different rejuvenators, except the aromatic-oil rejuvenator, which can be determined when the aging level of bitumen is known.

4.4.3. *Parameter SI and relative rejuvenation percentage SIR*

From the basic properties, there is a limited sulfur element in all rejuvenators, and thus no additional sulfoxide functional group is generated during the rejuvenation process. The variations of SI values of different rejuvenated bitumen as a function of rejuvenator content are summarized in Fig. 13. Similar to the CI parameter, the SI values of all rejuvenated binders exhibit a linear decreasing trend with the increase in rejuvenator dosage. Adding rejuvenators would enlarge the functional groups' overall quantity and dilute the sulfoxide terms' concentration ratio in the aged binder. For all rejuvenators, the SI values of rejuvenated bitumen enlarge as the aging grade of bitumen deepens. It manifests that the SI parameter is sensitive to the alteration of rejuvenator content and the aging grade of bitumen. Furthermore, the slope values of correlation formulas can be used to discriminate the impact of rejuvenator type, which also depends on the aging degree of bitumen. The difference in slope values of various rejuvenated

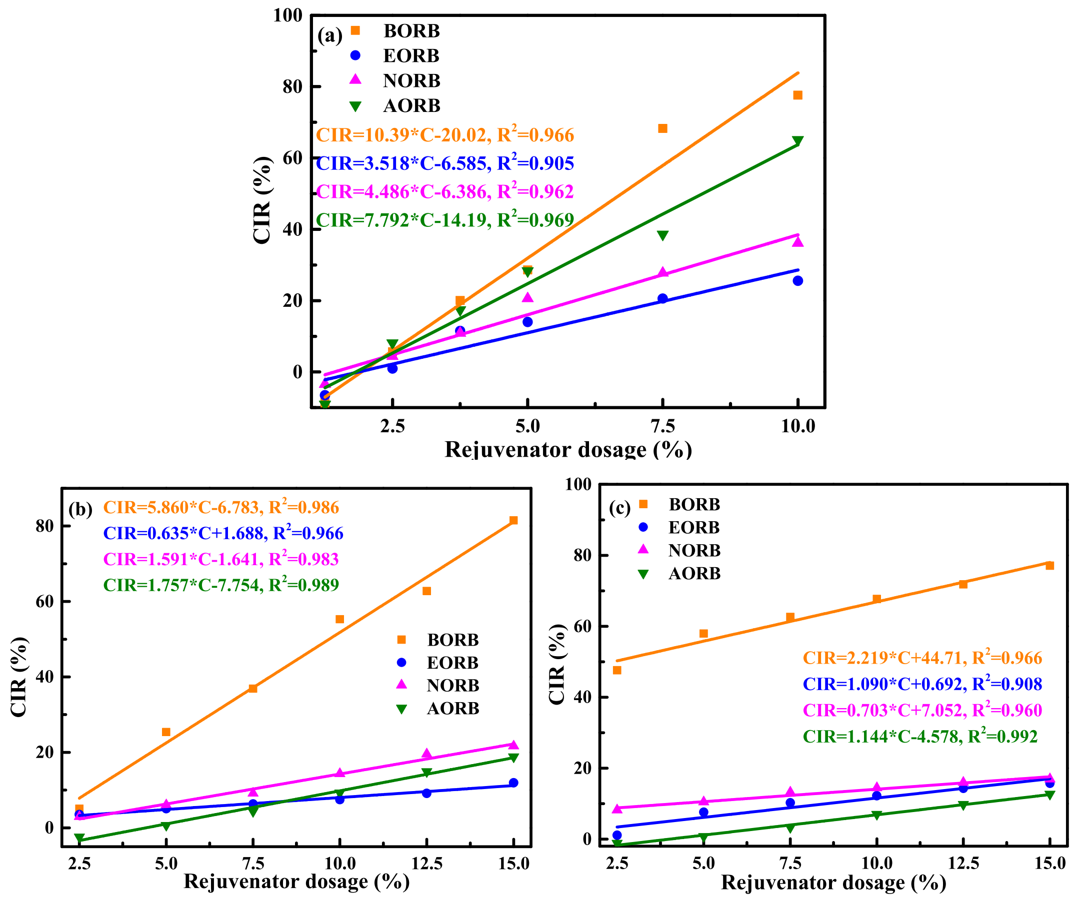

Fig. 11 – Variations of CIR parameter of rejuvenated bitumen versus rejuvenator dosage (a) LAB20; (b) LAB40; (c) LAB80.

binders is small in the LAB20 case, but the aromatic-oil effect on the SI parameter of LAB40 can be distinguished. When the aged bitumen is LAB80, there is a significant difference in the sensitivity of the SI parameter to rejuvenator concentration between various rejuvenated binders.

To quantitatively assess the coupling effects of rejuvenator type/dosage and aging grade of bitumen on the SI parameter of aged bitumen, the SI-based rejuvenation percentage SIR values of all rejuvenated bitumen systems are calculated following Eq. (12) and drawn in Fig. 14. It can be seen that the SIR values of all rejuvenated bitumen are positive, indicating that all rejuvenators exhibit restoration functions on the SI parameter of aged bitumen. Nevertheless, these SIR values are lower than 100%, and all rejuvenation conditions selected in this study fail to completely regenerate the SI parameter of aged bitumen to a virgin binder level. Moreover, the SIR parameter of the AORB binder is much lower than the other three kinds of rejuvenated binders. Hence, the aromatic-oil rejuvenator shows the weakest rejuvenation efficiency on the SI parameter of aged bitumen. The underlying reasons for the difference are complicated. According to GC-MS results, the aromatic-oil rejuvenator is rich in aromatic molecules (about 53.91%) with higher molecular weight and polarity. Little FTIR peaks represent the chemical characteristics of aromatic molecules (only at 1600 cm-1 for stretching vibration of C=C on the aromatic ring and fingerprint area), which results in a small increase in whole functional groups in AORB binders.

Conversely, the FTIR measurement is more sensitive to the variation of aliphatic molecules. For instance, two peaks at 2950 cm^{-1} and 2860 cm^{-1} representing the asymmetric and symmetric stretching vibrations of C–H on aliphatic hydrogen are very strong. Moreover, the peaks at 1460 cm^{-1} and 1375 cm^{-1} come from the bending vibration of C–H on methylene and methyl molecules, respectively. That's why the BO, EO, and NO rejuvenators, with a high percentage of long-chain aliphatic molecules, exhibit higher rejuvenation effects on the SI value of aged bitumen than the AO rejuvenator. The magnitude of SIR values of BO, EO, and NO rejuvenated binders strongly depends on the rejuvenator dosage and aging level of bitumen, especially the NORB binder. The difference in SIR parameters of BORB and EORB samples is also limited. It is challenging to differentiate the rejuvenation efficiency of bio-oil, engine-oil, and naphthenic-oil rejuvenators based on the SIR parameter, but it is valuable to identify the role of aromatic-oil rejuvenator. Interestingly, the finding is the opposite of the CIR case. Thus, it is recommended to amalgamate the SIR and CIR parameters for fully evaluating the rejuvenation efficiency of various rejuvenators on the chemical properties of aged bitumen with influence factors of rejuvenator type/dosage and aging grade of bitumen.

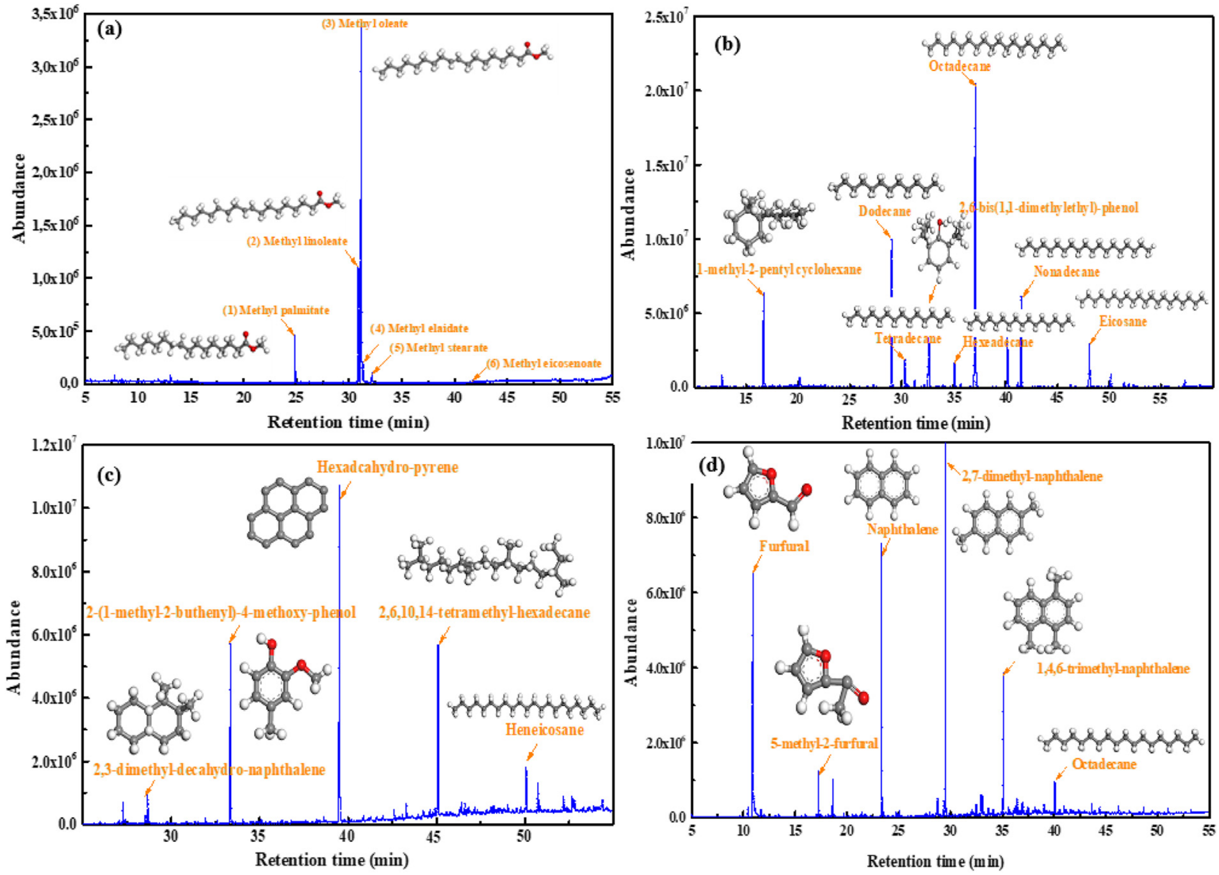

Fig. 12 – GC-MS results of four rejuvenators: bio-oil (a), engine-oil (b), naphthenic-oil (c), and aromatic-oil (d).

4.5. *Further discussion on critical parameters for rejuvenation efficiency evaluation*

This study involves four indicators (E_∞, δ, β, and τ) from the 2S2P1D constitutive model and two chemical indices (CI and SI) to estimate the influence of rejuvenator type/dosage and aging degree of bitumen on the rheological and chemical performance of rejuvenated binders. However, the rejuvenation efficiency of various rejuvenation conditions is also significantly affected by the type of evaluation indicators. To this end, one of the main objectives of this study is to examine the feasibility of various chemo-rheological indices on rejuvenation efficiency evaluation.

Fig. 15 illustrates a screening program for effective and critical evaluation indicators, which is available for all potential evaluation indicators in terms of chemical, physical, microstructural, thermodynamic, rheological, and mechanical properties. There are eight steps involved in this screening method. First, it is necessary to determine the potential indicators for rejuvenation efficiency evaluation together with their experimental results. Afterward, the rejuvenation possibility of these selected potential indicators should be checked, and these inapplicable indices with negative rejuvenation percentages will be excluded. To develop and optimize the rejuvenator components, the proposed evaluation indices must be sensitive to the influence of the rejuvenator type, and this work will be conducted in Step iii.

Similarly, it is necessary to consider the role of rejuvenator dosage during the selection of evaluation indicators, which will be abandoned if they fail to assess the effects of rejuvenator type and dosage on rejuvenation efficiency. Step v aims to examine the sensitivity of potential evaluation indicators to the aging level of bitumen. It is expected that the influence law of the rejuvenator type and dosage on the rejuvenation percentages of selected evaluation indicators is not dependent on the aging stage of bitumen. In the meanwhile, the effect of aging level should be reflected significantly. Thus, the evaluation indicators that do not meet the requirements of this step are defined as sensitive indices. In Step vi, the indicators still in compliance will be examined regarding the scope of rejuvenation percentage. In most studies, the ultimate purpose of adding rejuvenators is to restore the properties of aged bitumen to the virgin bitumen level. Thus, an expected scope of rejuvenation percentage is supposed to be 0–100% or properly a little more when a rejuvenation case shows a high rejuvenation efficiency. This step will rule out the incongruous index with abnormal rejuvenation percentage results. Eventually, these still-working parameters can be identified as effective evaluation indicators. Sometimes, several effective evaluation indicators are available, and it is essential to detect their internal correlations for proposing the critical evaluation indicators. With these key evaluation indices, it is easy and efficient to assess the rejuvenation efficiency of variable rejuvenation cases.

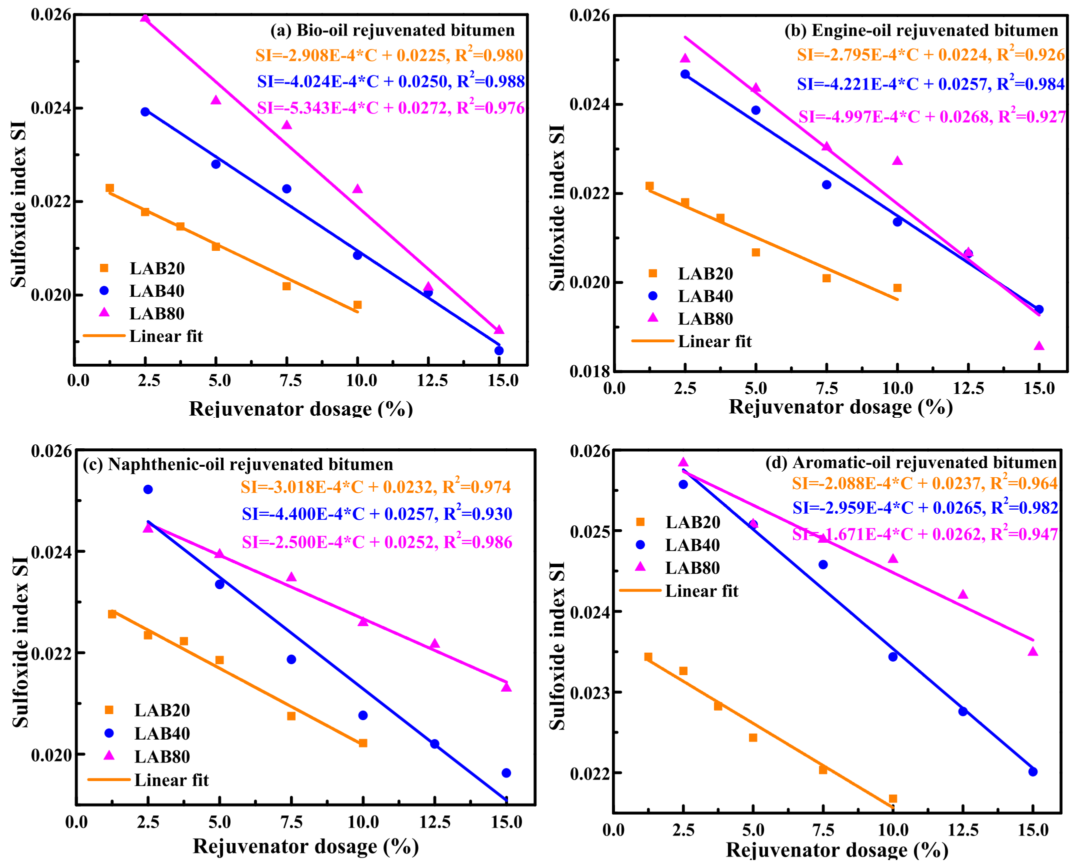

Fig. 13 – Variation of SI parameter of rejuvenated bitumen versus rejuvenator dosage.

It is difficult to consider all potential evaluation indicators at the same time. This study focuses on the rheological parameters from constitutive models and chemical indices from FTIR results. According to the experimental results discussed before, the analysis of critical constitutive models' parameters and chemical indices for rejuvenation efficiency evaluation is summarized in Table 5.

It should be noted that O and X represent the Yes and No, respectively. Meanwhile, some specific marks are explained as follows.

- **XO[1]:** Two rejuvenators (bio-oil and aromatic-oil) can restore the E_∞ value of aged bitumen, but the rejuvenation percentages of engine-oil and naphthenic-oil rejuvenated binders are negative.
- **XXO[2]:** The SI values of bio-oil, engine-oil, and naphthenic-oil rejuvenated binders are very similar, while only the SI parameter of aromatic-oil rejuvenated bitumen can be distinguished.
- **Ꙩ[3]:** The sensitivity of τ parameter to rejuvenator dosage depends on the scope of rejuvenator concentration. When the rejuvenator dosage is high, the τ-based rejuvenation efficiency τR values of all rejuvenated binders converge to 100%.
- **Ꙩ[4]:** The order for rejuvenation efficiency of bio-oil, engine-oil, and naphthenic-oil rejuvenated binders on the δ parameter keeps constant versus the aging level, while the δR values of aromatic-oil rejuvenated bitumen are strongly affected by the aging grade of bitumen.
- **Ꙩ[5]:** The magnitude for CIR values of BORB, EORB, and NORB binders is not dependent on the aging level of bitumen, while the CIR parameter of AORB varies a lot as a function of aging level.
- **XXO[6]:** With the increase in bitumen's aging level, the rejuvenation efficiency of aromatic-oil on the SI parameter of aged bitumen can be recognized consistently. However, the aging degree of bitumen significantly influences the magnitude of SIR values of BORB, EORB, and NORB binders.
- **0–800, 0-200[7]:** It is found that the scope of the δR parameter of bio-oil rejuvenated bitumen is 0–800%, while the δR values of EORB, NORB, and AORB are located in 0–200%.

In summary, no single evaluation indicator in this study meets all requirements shown in Fig. 15. Therefore, future research is needed to explore additional potential evaluation indices. Among the constitutive model parameters, the τ parameter is the most critical evaluation index, but its convergence characteristic may limit its usefulness in assessing the rejuvenation efficiency treated with high rejuvenator dosages. The δ parameter can serve as an auxiliary evaluation indicator to compensate for this limitation. Of the two chemical indices, the CI parameter is better than the SI parameter because the latter is not sensitive to rejuvenator type and is strongly influenced by the aging level of bitumen.

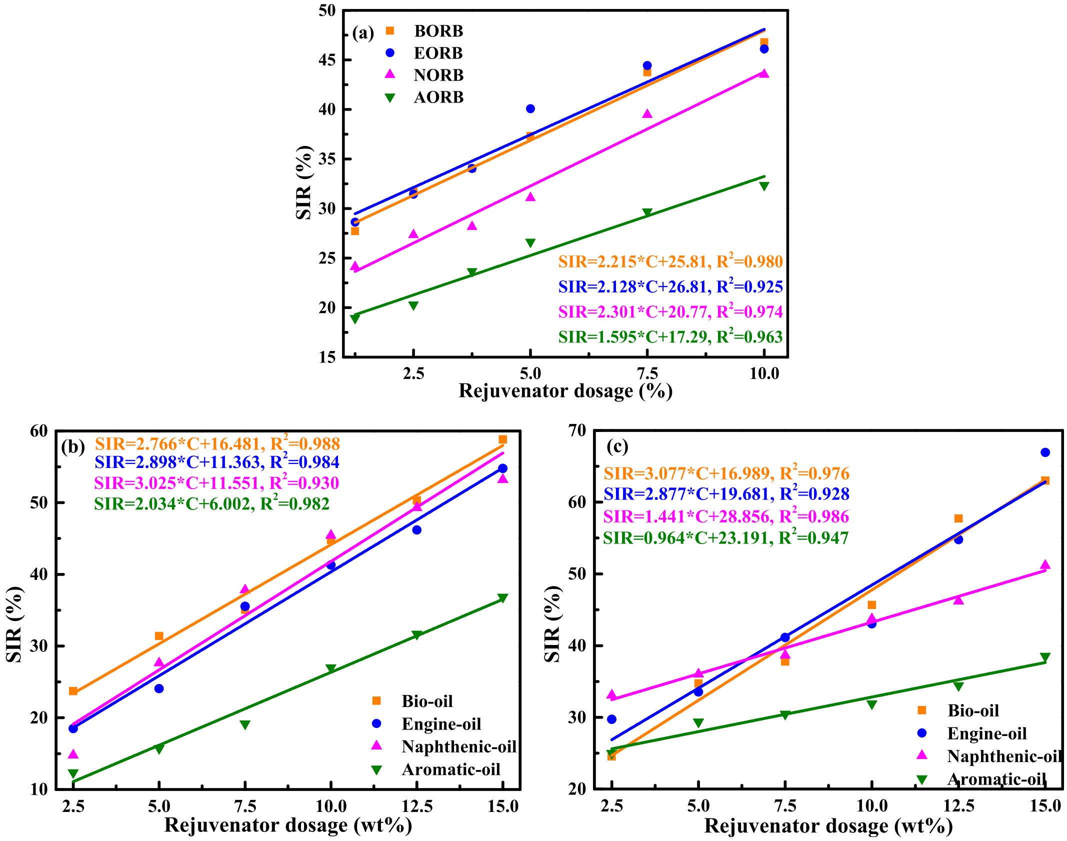

Fig. 14 – Variation of SIR parameter of rejuvenated bitumen versus rejuvenator dosage (a) LAB20; (b) LAB40; (c) LAB80.

However, the CI indicator may not be able to distinguish the rejuvenation effect of aromatic-oil rejuvenator from others due to its dependence on the aging level. To address this limitation, the SI parameter can be used as an auxiliary index. Therefore, the τ and CI parameters are critical evaluation indicators for assessing the rejuvenation efficiency of bitumen under various rejuvenation conditions, considering both micromechanics constitutive models and chemical characteristics.

4.6. *Potential connections between chemical indices and constitutive model parameters*

Researchers are interested in understanding the relationship between the chemical and rheological properties of bituminous materials to identify potential chemo-rheological models. Previous studies have shown a strong correlation between chemical indices from FTIR tests (such as carbonyl index and sulfoxide) and the rheological performance of virgin and aged binders. However, limited research has been conducted on the chemo-rheological correlations of rejuvenated binder with varying rejuvenation conditions. Rejuvenation introduces new chemical components (rejuvenator molecules), requiring consideration of different influence factors such as rejuvenator type, dosage, and aging stage of bitumen in chemo-rheological models of rejuvenated binders. This study is the first to explores the potential links between chemical indices (CI and SI) and constitutive model parameters (E_∞, δ, β, and τ) derived from rheological master curves.

The relationships between the chemical indices and rheological parameters of rejuvenated binders are explored in Fig. 16. The graph depicts linear relationships between the CI and four rheological parameters when considering only variations in rejuvenator dosage. This implies that the change rates of CI and rheological parameters are constant with respect to rejuvenator dosage. The corresponding linear correlation formulas are included. Thus, correlation equations and CI values can be used to predict micromechanical model parameters of rejuvenated binders with varying rejuvenator content. Additionally, the correlation curves for various rheological parameters are dependent on the rejuvenator type, which determines the correlation directions. Specifically, the E_∞ values of bio-oil and aromatic-oil rejuvenated binders linearly decrease with increasing CI parameter, while engine-oil and naphthenic-oil rejuvenated bitumen exhibit the opposite trend. The rejuvenator type does not have a significant impact on the correlation trends for the other three rheological parameters (δ, β, and τ).

The correlation curves between the chemical indices and rheological parameters of rejuvenated binders are more affected by the aging level of bitumen than by the rejuvenator type. When the aging level is the same, the correlation curves of various rejuvenated binders are similar. However, the curves shift distinctly when the aging level changes. The

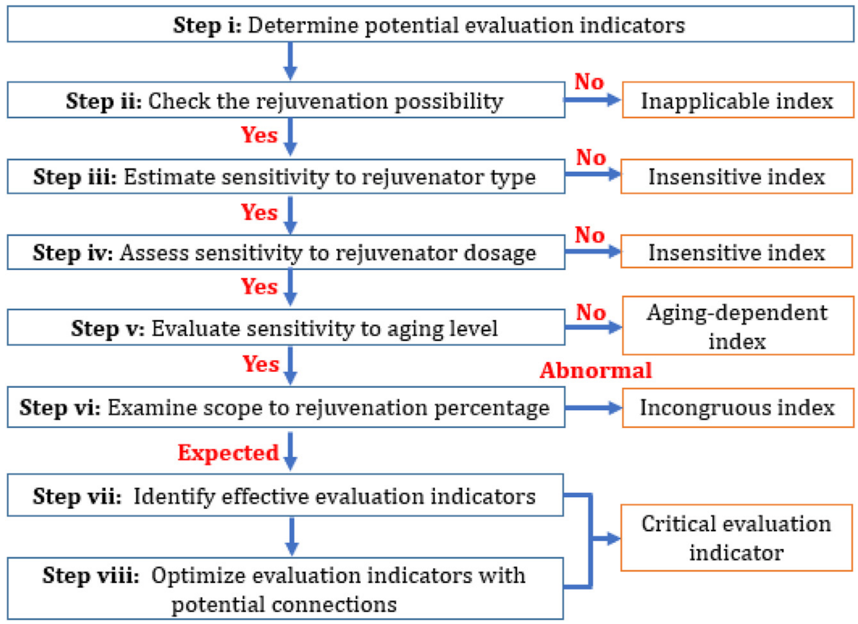

Fig. 15 – Screening program for effective and critical evaluation indicators.

impact of aging level on the correlation curves varies depending on the rejuvenator type and the selected rheological parameters. As the aging grade of bitumen deepens, the E_∞ and δ curves move to the bottom right, while the β and τ curves shift up to the right. However, the β curves of rejuvenated binders with LAB80 bitumen are not very sensitive and accurate. Moreover, the correlation curves of bio-oil rejuvenated bitumen are less sensitive to changes in aging level compared to other three rejuvenated binders, particularly for E_∞, δ, and τ parameters. The slope and intercept values in these correlation curves are influenced by both rejuvenator type and aging level of bitumen, and no conclusion can be drawn on this matter.

As previously stated, the effectiveness of rejuvenators varies depending on the evaluation indicator used. Fig. 17 illustrates the correlations between the rejuvenation percentages based on different rheological parameters and CI. Due to the difference in sensitivity to aging levels, the correlation curves for bio-oil rejuvenated binders are shown separately. The $E_\infty R$, δR, and βR vales of all rejuvenated binders exhibit linear correlations with the CIR parameter, while the τR values show exponential growth with an increase in CIR. For bio-oil rejuvenated binders, the range of abscissa and ordinate of correlation curves is larger than for other rejuvenators, indicating that bio-oil has the highest rejuvenation efficiency on both rheological and chemical properties of aged bitumen. The negative correlations between CIR and $E_\infty R$ of engine-oil and naphthenic-oil rejuvenated binders imply that the addition of EO and NO rejuvenators does not restore the E_∞ value of aged bitumen. Interestingly, the effect of aging level on the variation trend of $E_\infty R$ – CIR curves for BORB and AORB is opposite. As the aging level worsens, the $E_\infty R$ – CIR curves of BORB shift towards the bottom right, while those of AORB tend to move towards the upper left.

The δR parameters of all rejuvenated binders exhibit a linear increasing trend with an increase in CIR values, and BORB has the highest δR value magnitude, followed by EORB, NORB, and AORB. As the aging level deepening, EORB, NORB, and AORB show a trend of counter clockwise rotation in δR-CIR curves, while BORB exhibits a clockwise direction. Both rejuvenator type and aging grade of bitumen affect the correlation curves between the rejuvenation percentages based on rheological model parameters and CI, with rejuvenator type having a stronger influence. All rejuvenators have negative βR values, indicating their unfavourable impact on the restoration of aged bitumen's β parameter. When the aging degree increases from LAB20 to LAB40, the βR-CIR curves move down to the left for all rejuvenated binders. The exponential formula is feasible to τR-CIR curves of all rejuvenated binders, but these correlations significantly depend

Table 5 – Analysis of critical constitutive models' parameters and chemical indices.

Potential evaluation indicators	E_∞	δ	β	τ	CI	SI
Rejuvenation possibility	XO[1]	O	X	O	O	O
Sensitivity to rejuvenator type	O	O	O	O	O	XXO[2]
Sensitivity to rejuvenator dosage	O	O	O	ʘ[3]	O	O
Sensitivity to aging level	X	ʘ[4]	X	O	ʘ[5]	XXO[6]
Rejuvenation percentage scope (%)	−30-150	0-800, 0–200[7]	−400-0	0–100	0–100	0–70
Potential connections	To be studied in section 4.6					

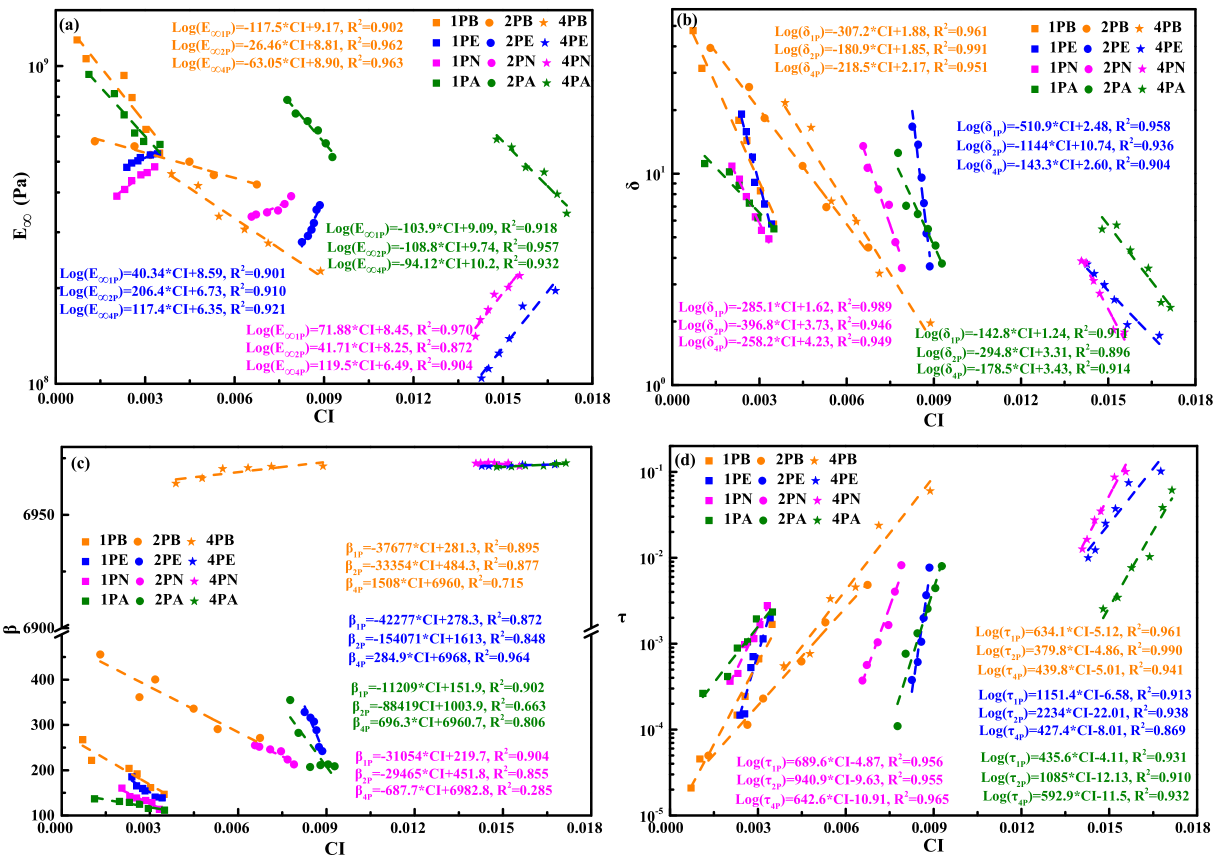

Fig. 16 – Connections between micromechanics models' parameters with carbonyl index of rejuvenated bitumen.

on the rejuvenator type and aging degree of bitumen. The τR values of BORB and EORB are higher than that of NORB and AORB binders, which agrees well with the conclusion based on βR-CIR curves. Moreover, the increasing aging level of bitumen accelerates the enlargement of τR values of rejuvenated binders, and the overall τR –CIR curves move upward. Further, the sensitivity of τR –CIR correlations to aging level are affected by rejuvenator type, and the corresponding magnitude is BORB < EORB < NORB < AORB. However, the influence intensity of rejuvenator type and aging level on τR –CIR curves of various rejuvenated binders weaken as the aging degree increases.

Fig. 18 depicts the correlation curves between the constitutive model parameters and SI. The results show a good linear relationship between the 2S2P1D model indicators and SI. However, these correlation curves are highly sensitive to the rejuvenator type, the aging level of bitumen, and the type of rheological index. The E_∞ values of BORB and AORB binders reduce linearly with the increase in SI, while the E_∞ parameters of EORB and NORB show positive correlations with SI. Moreover, the E_∞ – SI curves of all rejuvenated binders tend to move downward as the aging level deepens from LAB20 to LAB40 and LAB80. It can be concluded that the aging level's influence on the E_∞ – SI curves of AORB is lower than the other three rejuvenated binders based on the difference in spacing.

As the SI value increases, the δ parameters of all rejuvenated bitumen decrease linearly. However, the spacing between δ-SI curves of various rejuvenated binders is limited, indicating that the influence of rejuvenator type and aging degree on δ-SI curves of rejuvenated bitumen is less significant than on δ-CI curves. The sensitivity of δ-SI curves of EORB and NORB to aging level is greater than that of BORB and AORB, with the δ-SI curves of EORB and NORB moving down dramatically when the aging level deepens from LAB40 to LAB80. Interestingly, the δ-SI curves of EORB and NORB with LAB80 are similar, indicating that the difference in influence between engine-oil and naphthenic oil on δ-SI curves reduces significantly with increased aging level.

For rejuvenated binders with LAB20 and LAB80, the β values decline linearly as SI increases. Both the rejuvenator components and aging level strongly affect the β-SI curves, influencing the slope and intercept terms of correlation equations. As for the τ-SI curves, a positive and linear increasing trend is observed, with a clear difference in τ-SI curves of rejuvenated bitumen with various rejuvenator types and aging degrees. However, it is difficult to separate their effects on the slope and intercept values of correlation equations. As the aging degree aggravates, the slope values of rejuvenated binders reduce, while the intercept parameter increases gradually. Similar to δ-SI results, a high aging level

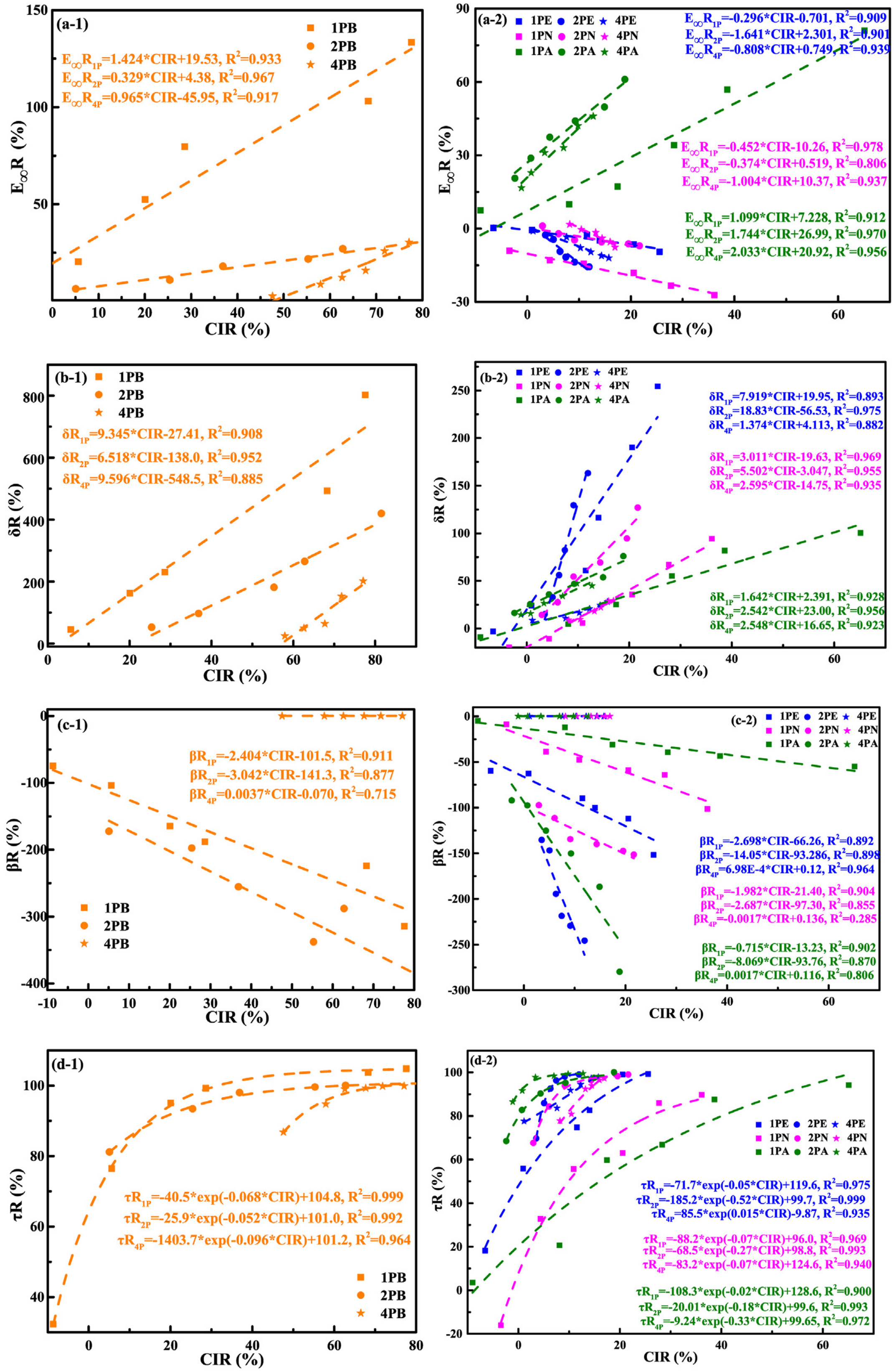

Fig. 17 – Connections between rejuvenation percentages derived from micromechanics models' parameters and carbonyl index of rejuvenated bitumen.

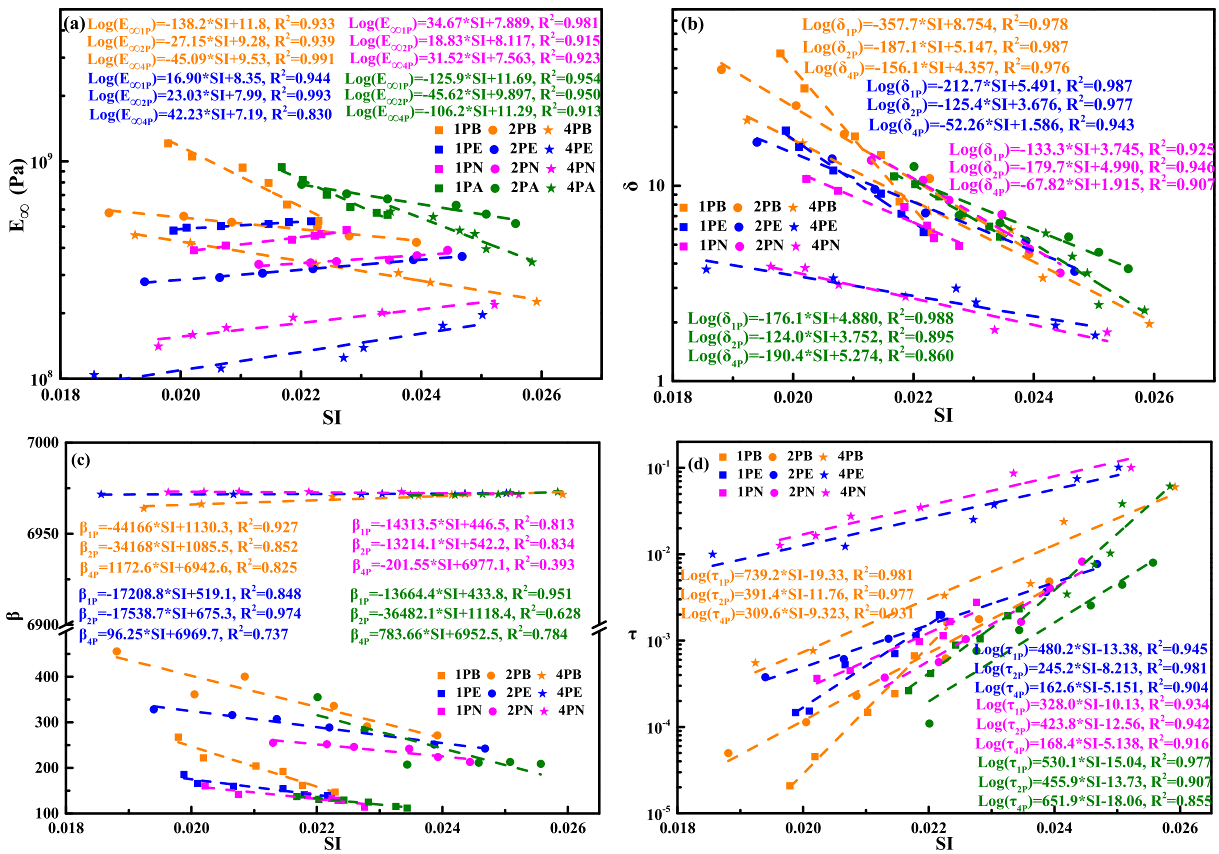

Fig. 18 – Connections between micromechanics models' parameters with sulfoxide index of rejuvenated bitumen.

(LAB80) shows a significant impact on the τ-SI correlation curves of engine-oil and naphthenic-oil rejuvenated bitumen, while their correlation equations at that stage are much closer.

In Fig. 19, the correlation curves between SIR and $E_\infty R$, δR, βR, and τR values of different rejuvenated binders are presented. The $E_\infty R$ values of bio-oil and aromatic-oil rejuvenated bitumen enlarge linearly with an increase in the SIR parameter. However, the engine-oil and naphthenic-oil rejuvenated binders show a converse phenomenon, indicating that the $E_\infty R$ parameter is not effective to evaluate the rejuvenation efficiency of EO and NO rejuvenators. The BORB binder has a higher $E_\infty R$ value than the AORB, and the slope values in their $E_\infty R$-SIR curves decrease first and increase slightly with an increase in the aging grade of bitumen. Conversely, the corresponding intercept parameter shows an opposite trend. For EORB and NORB binders, their $E_\infty R$-SIR curves experience a counter-clockwise transfer as the aging level increases. Specifically, the slope value gradually increases, and the intercept parameter first drops and then increases. However, the aging effect on the $E_\infty R$-SIR curves of EORB and NORB is less significant than for BORB and AORB.

The δR values of BORB and AORB are larger than those of EORB and NORB, and they increase linearly with the SIR parameter. As the aging level of bitumen increases, all δR-SIR curves rotate clockwise due to the decreasing slope values. It is worth noting that the δR-SIR curves of EORB and NORB binders overlap when the aged bitumen is LAB20. Therefore, EO and NO rejuvenators exhibit a similar rejuvenation efficiency on the δ and SI indicators of severely aged bitumen. Similar to the βR-CIR case, only the βR-SIR curves of rejuvenated bitumen with LAB20 and LAB40 are discussed, and the negative βR values show that all rejuvenators cannot restore the β parameter of aged bitumen, making the βR index an inefficient evaluation indicator for rejuvenation efficiency. Nevertheless, all βR values still show an extremely linear correlation with the SIR parameter. When the aged bitumen changes from LAB20 to LAB40, the slope and intercept values of correlation equations decline dramatically, especially for AORB. Thus, the βR-SIR curves of rejuvenated binders are jointly determined by rejuvenator type and aging degree, while the influence level of rejuvenator components is relatively lower. Lastly, the τR-SIR curves of various rejuvenated bitumen can be well fitted by an exponential equation. The combined influence of rejuvenator type and aging level on these τR-SIR curves can be detected, but it becomes less noticeable as the rejuvenator dosage increases since the SIR values tend to converge at 100%. The difference in τR-SIR curves of different rejuvenated binders is smaller than τR-CIR curves, further validating that the CI parameter is more efficient evaluation indicator than the SI. When the aging level of bitumen exacerbates from LAB40 to LAB80, the difference in τR-SIR curves is limited, especially for BORB. Therefore, the influence level of aging status weakens when the bitumen is severely aged.

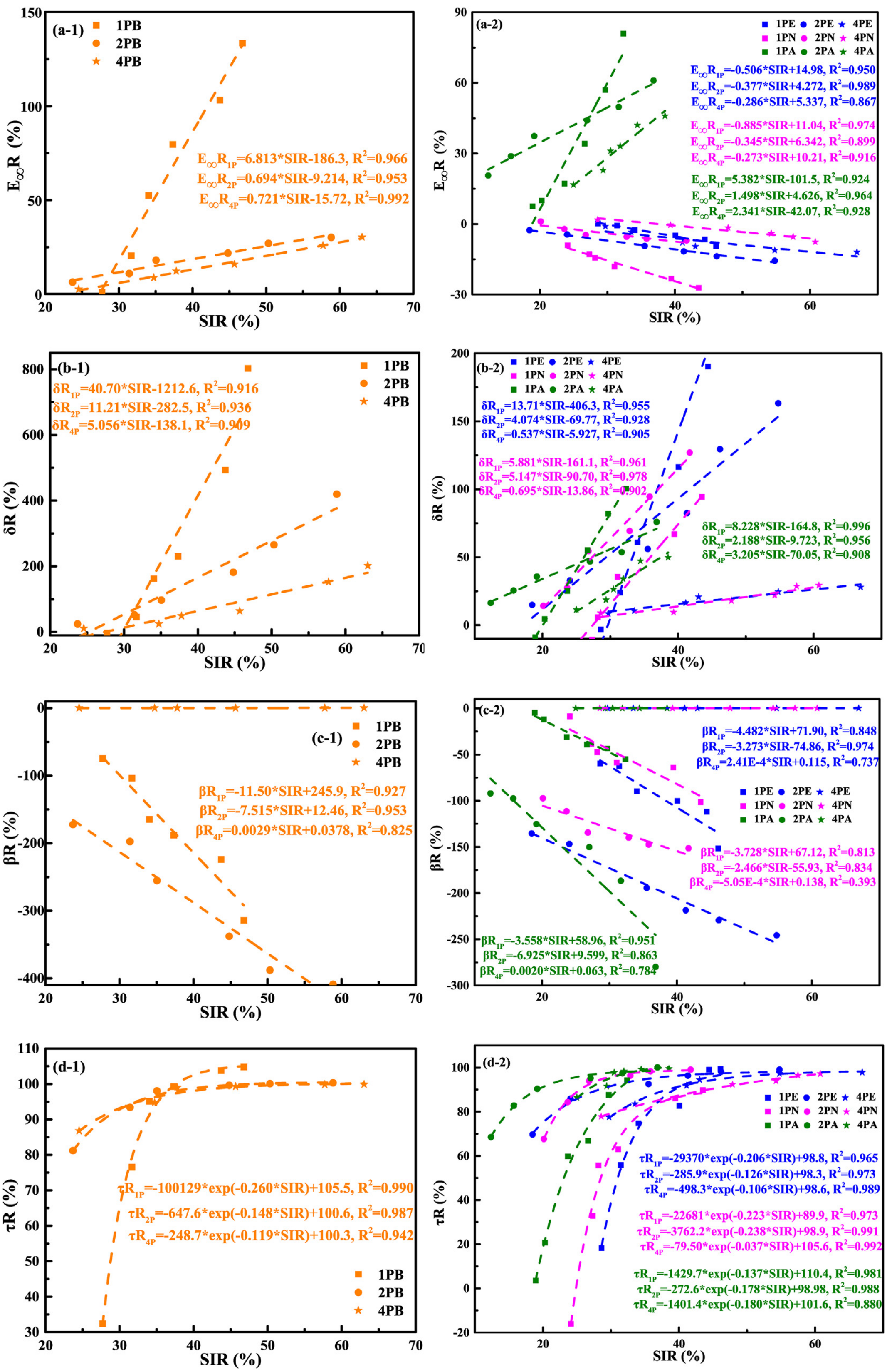

Fig. 19 – Connections between rejuvenation percentages derived from micromechanics models' parameters and sulfoxide index of rejuvenated bitumen.

5. Conclusions and recommendations

The study proposes critical parameters of rejuvenation efficiency evaluation for different rejuvenation cases, based on rheological constitutive models and chemical properties. The potential connections between micromechanics model parameters and chemical indices, as well as their rejuvenation percentages, are explored.

(1) The constitutive 2S2P1D model is adopted to describe the G* and δ master curves of the virgin, aged, and rejuvenated binders. Four parameters (E_∞, δ, β, and τ) derived from 2S2P1D models correlate well with rejuvenator dosage linearly, with a strong dependence on rejuvenator type and aging degree of bitumen.

(2) The rejuvenation potential is affected the selected evaluation indicators based on rejuvenation percentages. The involvement of rejuvenators can restore the δ, τ, CI, and SI values of aged bitumen towards a virgin bitumen level. However, the E_∞ parameter is not applicable to assess rejuvenation efficiency of engine-oil and naphthenic-oil rejuvenators, although the positive $E_\infty R$ values of bio-oil and aromatic-oil rejuvenated bitumen are detected. Moreover, all rejuvenators fail to restore the β parameter of aged bitumen.

(3) A screening program is proposed for distinguishing the effective evaluation indicators on rejuvenation efficiency of various rejuvenation cases considering the coupling influence of rejuvenator type, dosage, and aging level of bitumen. Ultimately, the τ and CI parameters are selected as critical evaluation indicators from the perspective of micromechanics constitutive models and chemical characteristics.

(4) Linear correlations between all rheological parameters (E_∞, δ, β, and τ) and chemical indices (CI and SI) are observed and established. In addition, their rejuvenation percentages are connected linearly (E_∞, δ, β) and exponentially (τ). However, the goal of establishing a unified chemo-rheological correlation curve for all rejuvenation cases in this study cannot be achieved because of a strong dependence on rejuvenator type and aging level of bitumen.

This study's findings lead to the following recommendations for future work.

(i) To propose an effective ad thorough standard for evaluating rejuvenation efficiency, more rheological and chemical parameters should be involved in addition to micromechanics models' parameters and two FTIR indices focused on in this study.

(ii) While rheological and chemical characterizations were conducted in this study to evaluate rejuvenation efficiency, exploring the underlying mechanism for the difference in rejuvenation efficiency of variable rejuvenation conditions may require the adoption of more multi-scale methodologies in the future.

(iii) More advanced data analysis methods, like machine learning, are expected to explore the complex correlations between chemical, thermodynamic, microstructural, and rheological indicators.

(iv) Investigating more varied rejuvenation cases would further validate and optimize the critical evaluation indicators proposed here, as only four rejuvenator types and three aging level cases were involved in this study, which is sufficient but incomplete.

Credit authorship contribution statement

Shisong Ren: Methodology, Investigation, Formal analysis, Writing-original draft, Writing-review and editing. Xueyan Liu: Supervision, Writing-review and editing. Aikaterini Varveri: Writing-review and editing. Sadaf Khalighi: Investigation, Writing-review and editing. Ruxin Jing: Methodology and Supervision. Sandra Erkens: Methodology and Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmrt.2023.06.005.

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