The short-term aging effects of Polyvinyl Chloride (PVC) and Nano Silica (NS) as modifiers on asphalt binders

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Tác dụng chống lão hóa ngắn hạn trong bê tông nhựa của Polyvinyl Clorua (PVC) và Nano Silica (NS) khi được sử dụng làm chất cải tính

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ABSTRACT

Many studies have shown that for a pavement paved with an asphalt-aggregate mixture, to achieve its design life, the asphalt mustn't age too hard during storage, during the production process, or while on the road. The short-term aging effects of Polyvinyl Chloride (PVC) and Nano silica (NS) as modifiers on asphalt binders were investigated. The physical properties, penetration, softening points, viscosity measurements, dynamic shear rheometer (DSR), and multiple stress creep recovery (MSCR), under the aging conditions of unmodified and modified asphalt were determined for various PVC and NS contents. To simulate the aging in a short term in the laboratory, the rolling thin film oven test was conducted. Obtained results indicated that adding 5% PVC and 1% NS had a significant positive effect on the aging resistance of asphalt binder through increasing 59.49% penetration aging ratio (PAR) values. It was also observed that adding PVC and NS reinforced the aging resistance of the asphalt binder. Nevertheless, adding PVC and NS reduced softening point increment (SPI), viscosity aging index (VAI), as well as rutting factor aging index (AIR). The asphalt binder modified with PVC/NS demonstrated better performance compared to the asphalt binders only modified with PVC or NS. The results of this study demontrate the feasibility of applying the PVC/NS combination treatment to asphalt in practical applications.

Từ khóa:
Chất kết dính nhựa đường, lão hóa ngắn hạn, máy đo lưu biến cắt động, Nano Silic, Polyvinyl clorua.

TÓM TẮT

Nhiều nghiên cứu cho thấy đối với mặt đường bê tông nhựa, để đạt được tuổi thọ thiết kế thì điều quan trọng là nhựa đường không được lão hóa quá cứng trong suốt thời gian bảo quản, trong quá trình sản xuất hoặc trong thời gian lưu hành trên đường. Tác dụng chống lão hóa ngắn hạn trên nhựa đường của chất cải tính Polyvinyl Clorua (PVC) và Nano silica (NS) đã được nghiên cứu. Để mô phỏng quá trình lão hóa trong thời gian ngắn trong phòng thí nghiệm, bài báo đã sử dụng lò cán nóng màng mỏng (RTFO) để mô phỏng kiểm tra. Tiến hành thêm chất cải tính với hàm lượng PVC và NS khác nhau để kiểm nghiệm các đặc tính vật lý: độ kim lún, điểm chảy dẻo, độ dính bám, đặc tính lưu biến cắt động (DSR) và khả năng phục hồi từ biến do ứng suất đa dạng (MSCR), của nhựa đường nguyên chất và nhựa đường cải tiến chưa lão hóa và đã lão hóa. Kết quả cho thấy việc bổ sung PVC và NS có tác dụng tăng cường khả năng chống lão hóa của chất kết dính nhựa đường. Sự kết hợp của 5% PVC và 1% NS làm gia tăng trị số tỷ lệ lão hóa xuyên thấu (PAR) lên 59,49%, có tác động tích cực đến khả năng chống lão hóa của nhựa đường. Tuy nhiên, việc bổ sung PVC và NS làm giảm mức tăng chỉ số điểm hóa mềm (SPI), chỉ số lão hóa độ nhớt (VAI), cũng như chỉ số lão hóa hệ số hằn lún (AIR). Bê tông nhựa được cải tính kết hợp bằng PVC/NS có hiệu quả sử dụng tốt hơn bê tông nhựa chỉ được cải tính bằng PVC hoặc NS. Kết quả bài báo này chứng minh tính khả thi của việc áp dụng kết hợp đồng thời chất cải tính PVC/NS cho bê tông nhựa trong các ứng dụng thực tế.

1. INTRODUCTION

Asphalt is one of the oldest materials in the paving industry. Using polymers have shown successful results as modifiers of asphalt binder. Various polymer modifiers can give different properties of composite materials. Recently, the most problematic plastics currently produced is polyvinyl Chloride (PVC). Nowadays, the annual output of PVC in the world exceeds 20 million tons, which is higher than 3 million tons in 1965 [1, 2]. Over the years, waste PVC products have been the main cause of incineration of dioxins in incinerators [3]. Using PVC in the pavement technical not only protects the environment and reduces the cost of pavement production but also enhances the physical properties of asphalt binder [4]. When PVC is used to modify asphalt, it can improve the stiffness of asphalt pavement and reduce the deformation of asphalt pavement under heavy traffic load at high temperatures [5].

The Nano silica SiO_2 (NS) material is also widely used as an inorganic additives to improve the properties of the asphalt binder. In the last ten years, the NS has attracted much attention from pavement researchers for preparing asphalt materials because it has perfect stability, high specific surface area, chemical purity, strong adsorption, and good dispensability [6, 7]. At high temperatures, NS has marvelous properties in strength, toughness and thermal. Ramez et al. reported that using NS material as a modifier has a convincing effect on the different properties of the asphalt binder and can build durable pavements and reduce the cost of the pavement life cycle [8].

The aging of asphalt, existing during the production, mixing, transportation, and the whole of binder service life is a very complicated process [9, 10]. The aging of asphalt makes asphalt hard but easily broken, and the pavement is vulnerable to break [11, 12]. Using modifiers with polymer and nano materials have some improvement in the anti-aging properties of asphalt [13, 14]. Recently, a few researchers published their results about the chemical composition and rheological properties of modified asphalt under different aging conditions. Therefore, the objective of this study was to report that modified asphalt with combined PVC and NS had an important positive effect on the aging process, which no researchers reported before. This study does not only provide useful information for the anti-aging asphalt paper but also helpful guidance for the operation of the asphalt industry.

2. RESEARCH METHODS

2.1. Materials and sample preparation

The base asphalt selected in this research was AH-70 asphalt, and the characteristics of the base asphalt are shown in Table 1.

Table 1. Physical and mechanical properties of asphalt binder used in this study

Test	Standard	Result
Penetration (100 g, 5s, 25 °C), 0.1 mm	ASTM D5	75.5
Ductility (25 °C, 5 cm/min), cm	ASTM D113	150+
Softening point (°C)	ASTM D36	48.7
Rotation viscosity (135 °C, Pa.s)	ASTM D4402	0.581
Specific gravity at 25 °C (g/cm^3)	ASTM D70	1.03
Flash point (°C)	ASTM D92	320

PVC polymer was used as the asphalt modifier in this study; its basic properties are presented in Figure 1 and Table 2.

Figure 1. Polyvinil Clorude (PVC)

Table 2. Physical and mechanical properties of PVC used in this study

Appearance	Softening point (°C)	Melting point (°C)	Density (g/cm³)	Tensile strength (MPa)
White	80	170	1.42	60

Shanghai New Materials Co. Ltd offers the nano-silica; its basic properties are listed in Figure 2 and Table 3.

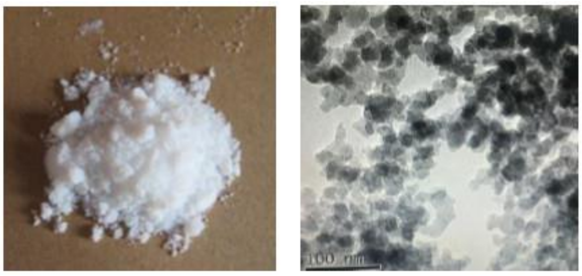


Figure 2. Nanosilica (NS) sample

Table 3. Properties of nano silica SiO_2 sample used in this study

Type	Appearance	Average grain size (nm)	Specific surface area (m²/g)	pH value
SP15	White	15 ± 5	250 ± 30	5-7

The PVC and NS (PN) prepared by the melt blending method is simple and efficient. One 5% concentration of PVC and three concentrations (1.0%, 2.0%, and 3.0%) of NS were produced. Firstly, the asphalt (about 500g) was heated to 180°C, and PVC was added to it at 170°C and mixed for 15 min at a shearing rate of 1200 r/min. Secondly, the mechanical mixing of PVC lasts for 60 min at 4000 r/min at 180°C. Finally, NS with different concentrations was added to the mixture and sheared together at 160°C for 45 min at a speed of 3500 r/min.

2.2. Methods

Penetration, softening point, RV viscosity, dynamic shear rheometer (DSR), and multiple stress creep recovery (MSCR) experiments were conducted on the base and modified asphalt. In each type of binder selected three samples were measured, and their average values were taken into account.

The DSR PG was graded by the MCR 702 dynamic shear rheometer produced by Anton Par Company. DSR tests were conducted over a range of temperatures: 52, 58, 64, 70, and 76 ^oC; loading frequency of 12 rad/s for unaged binder and 10 rad/s for aged binder; using small plates with diameters of 25mm for 1mm thickness samples.

The standard Rolling thin film oven (RTFO) experiment was implemented to produce the short-term aging of the asphalt binder. The unaged asphalt was heated during rolling at 163^oC for 85 minutes. In this research, aging indices were calculated in formulas (1), (2), (3), and (4) [1]

SPI = Softening pointaged - Softening pointunaged (1)

$$PAR = \frac{Penetration_{aged}}{Penetration_{unaged}} \quad (2)$$

$$VAI = \frac{Viscosity_{aged} - Viscosity_{unaged}}{Viscosity_{unaged}} \quad (3)$$

$$AIR = \frac{G^*/\sin(\delta)_{aged}}{G^*/\sin(\delta)_{unaged}} \quad (4)$$

where,

SPI: softening point increment;

PAR: penetration aging ratio;

VAI: viscosity aging index;

AIR: the aging index of the rutting factor (G*/sin(δ)).

The MSCR experiment was conducted using the DSR machine according to AASHTO T350-14. It measured the permanent deformation properties of all types of asphalt binders under aging conduction. Two standard stress levels 100 Pa and 3200 Pa were applied to the all kinds binder. Each stress level consisted of 1s shear creep followed by a recovery period of 9s, a totally of 200s for 20 cycles. Both recovery percentage (R) and non-recoverable compliance (Jnr) were conducted with MSCR. (R) and (Jnr) (letter notation) were determined from Eq (5-8) (ASTM D2872, 2015) and then they were calculated average results from 10 cycles:

$$R_T(T, N) = \frac{\varepsilon^N_r}{\varepsilon^N_t}.100 \quad (5)$$

$$R(T) = \frac{1}{10}\sum_{N=1}^{10} R_T(T,N) \quad (6)$$

$$J_{nr}(T, N) = \frac{\varepsilon^T_{nr}}{3200} \quad (7)$$

$$J(T) = \frac{1}{10}\sum_{N=1}^{10} J_T(T,N) \quad (8)$$

where,

ε_r: recoverable deformation;

ε_t: total deformation;

ε_{nr}: non-recoverable deformation;

T: is the applied shear stress;

N: 1, 2… 10: the loading cycle number.

In this paper, tests were performed at five temperatures 52, 58, 64, 70, and 76 ^oC.

3. RESULTS AND DISCUSSION

3.1. Penetration

Penetration represents the consistency of the material and reflects the rheological properties of asphalt binder. Figure 3 displays the effect of PVC, NS, and PN on the penetration of modified asphalt under short-term aging. Adding PVC, NS, and PN made the penetration value of virgin asphalt decrease significantly. The measured penetration depth of asphalt decreased by 29% at a 1%NS content, by 49.53% at a 5%PVC content, by 60% at the (5%PVC + 1%NS) content. The penetration depth of PN modified asphalt binder was lower than those of PVC and NS modified binders, the lowest penetration depth value at 5P3N. Furthermore, the asphalt samples modified with PN represented continuously the penetration decreased continuously for unaged and RTFO aged asphalt. The anti-aging property of asphalt was strengthened after addition of PVC and NS.

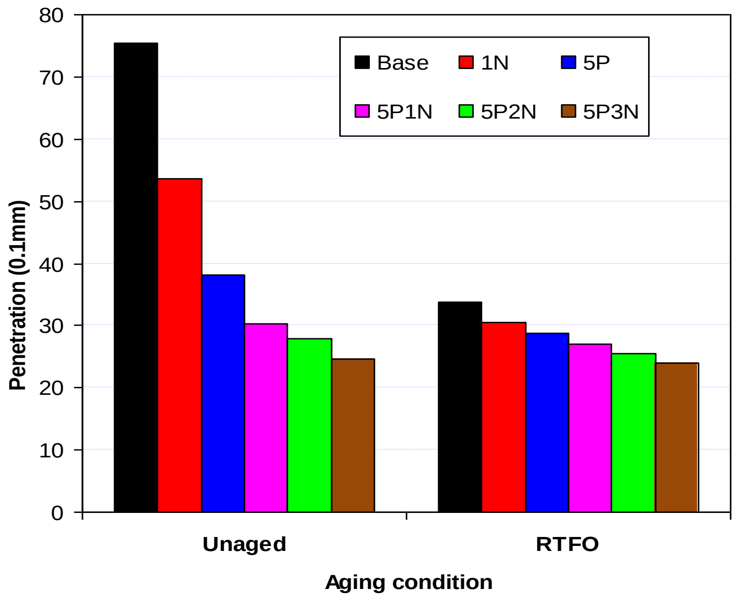


Figure 3. Penetration of asphalt binder with different PVC and NS contents

3.2. Softening point

Softening points describe the high temperature stability of asphalt in the laboratory. Normally, a high softening point means that the asphalt possesses high-temperature stability. Figure 4 shows the effects of PVC and NS concentration on the softening points of modified asphalt before and after short-term aging. The softening point of base asphalt climbed from 48.7°C to 55.85°C after RTFO aging, respectively. The softening point increased with the increase in NS content, even though the increment was minor at all concentrations, the highest value was 5P3N. The combined modification of PVC and NS increased the softening point value, indicating that adding PN improved the stability of asphalt under high-temperature.

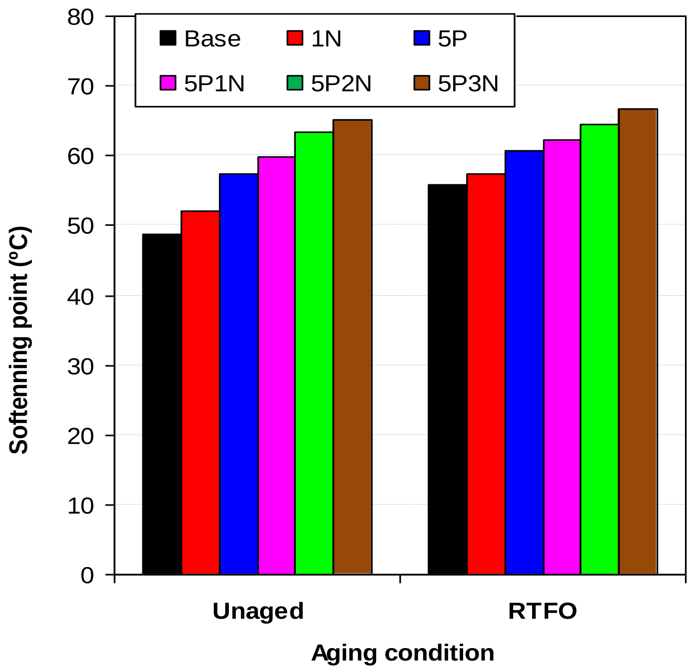


Figure 4. Softening point of asphalt binders with different PVC and NS contents

3.3. Rotational Viscosity

The rotational viscosity reflects the flow property of the binder. Figure 5 illustrates the rotational viscosities at the temperature range from 135°C to 175°C for the base asphalt and PVC, NS, PN modified binder at different concentrations of NS. It is clearly shown that the viscosity of all binders decreases with increasing temperature. The viscosity of asphalt of both PVC and NS was higher than the viscosity of base asphalt (the rotational viscosity value from 800 to 1400 mPa.s). The standard in Super pave specification obligates that the viscosity of the used asphalt binder must not be higher than 3000 mPa.s. These results show that, when adding PVC, NS or mixture of PVC and NS to base asphalt, the rotational vicosity of the asphalt will increase, which is vital in increasing the binder film thickness for coating aggretate in the hot mixture. Therefore, the high viscous asphalt mixute will maintain the stability of asphalt mixture [9]. The rotational viscosity values became highest at the ratio 5P1N.

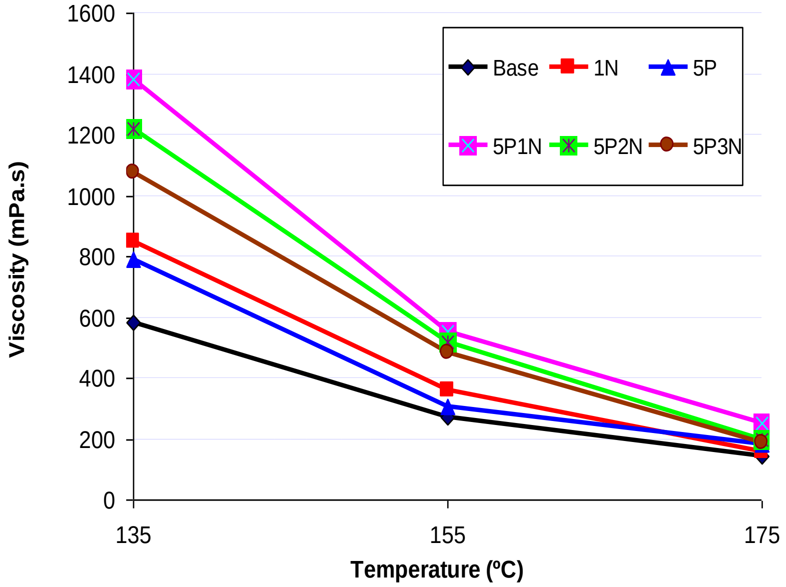
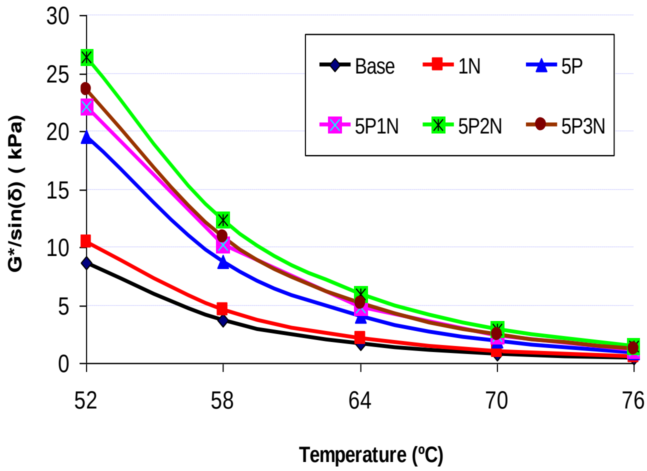


Figure 5. Relationship between the binder viscosity and modifier contents

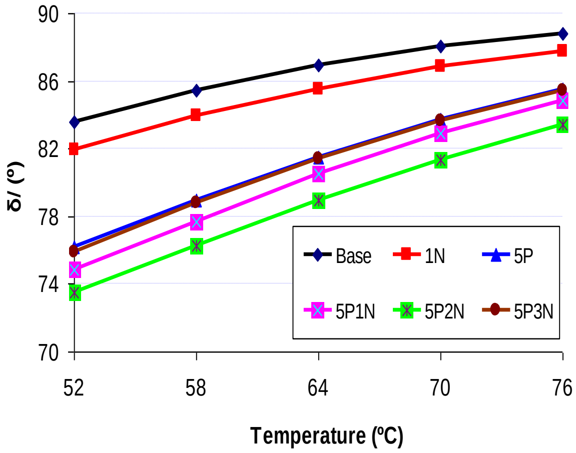
3.4. Dynamic shear rheological tests

DSR experiment is typically performed to show an asphalt binder resistance to rutting at high temperatures by measure the G*/sin(δ) value. The asphalt binder has to be flexible and sufficient to prevent rutting. The value of G*/sin(δ) illustrates the performance grade of asphalt [15]. Figures 6 and 7 represent the rutting parameters of PVC, NS and PN measured at temperatures of 52, 58, 64, 70 and 76°C before and after RTFO aging. They display that the excellent of G*/sin(δ) increases with increasing concentrations of modifiers. Moreover, the G*/sin(δ) values obtained of the PVC- and PN- modified asphalt were higher than NS-modified asphalt. It is meaning the PVC- and PN-modified asphalt binders have higher anti-rutting than their NS counterparts. In particular, binders 5P2N display the highest rutting factor values, higher than 3 times and 2 times as compared to base asphalt before and after RTFO aging. Overall, the result all of the modified asphalt prove that PN- modified asphalt possesses the highest anti-rutting. Therefore, Using PN-modified in high-temperature place to achieve the best asphalt binder performance.

The change in phase angle can be used to assess the anti-aging of RTFO test aged modified asphalt. The decrease in phase angle δ enhances the elastic reply of the asphalt and mixture flexibility. As shown in Figure 6-7, the phase angle δ of all RTFO aged binder is much lower than that of their virgin asphalt. On the other hand, the phase angle δ value of series "Base" from 78° to 87° but it decreases from 67° to 78° in series "5P". In the mean time series "5P2N" have the lowest phase angle value among of all type asphalts. This indicates that the modified asphalt possesses a more elastic structure after RTFO aging and could enhance the asphalt binder's anti-rutting property.

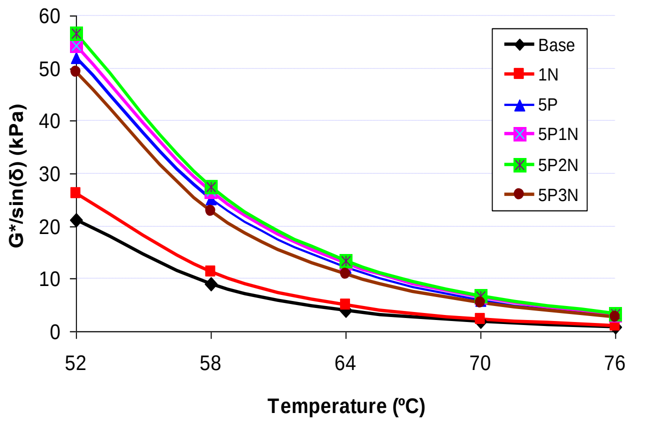


(a) Unaged

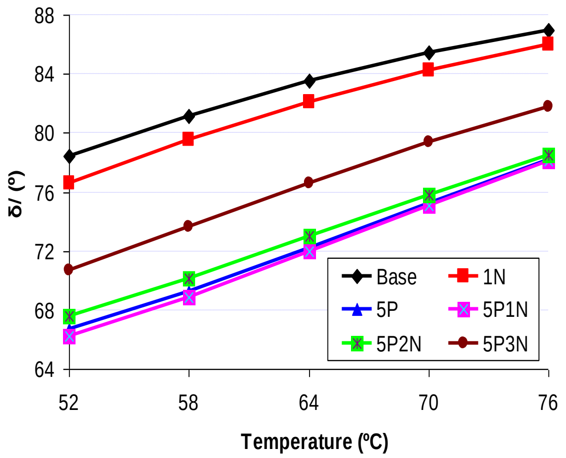


(b) Unaged

Figure 6. G*/sin(δ) and (δ) of unaged binder



(c) RTFO aged



(d) RTFO aged

Figure 7. G*/sin(δ) and (δ) of RTFO aged binder

3.5. Multiple stress creep recovery

J_{nr}(3.2) predominantly characterizes the anti-rutting of asphalt binder, and typically a higher J_{nr}(3.2) value represents a lower rutting performance. Figure 8(a) shows that the J_{nr} values for all the asphalts decrease with using PVC, NS, and PN- and increase in temperature. On the other hand, in areas of rutting resistance the 5P3N binder illustrates the best performance, and the base asphalt ranks the lowest.

The measures R(3.2) indicate for evaluating the delayed elastic conduct of asphalt binder. A larger R can be translated into a larger capacity of bitumen to recover from deformation tested with the load application. As usual, under most cases of testing temperatures and adding PVC, and NS contents, the kind of asphalt performed the best is 5P3N. It is meaning, it has got the greatest elastic structures when submitted to creep-recovery loading alignments (Figure 8 (b)). The virgin asphalt is surveyed to exhibit the lowest recovery properties at all temperatures.

This result suggests that the addition of PVC and NS improve the elastic response of virgin binder; and enhances the capability of anti-rutting under repeated loads of asphalt binder.

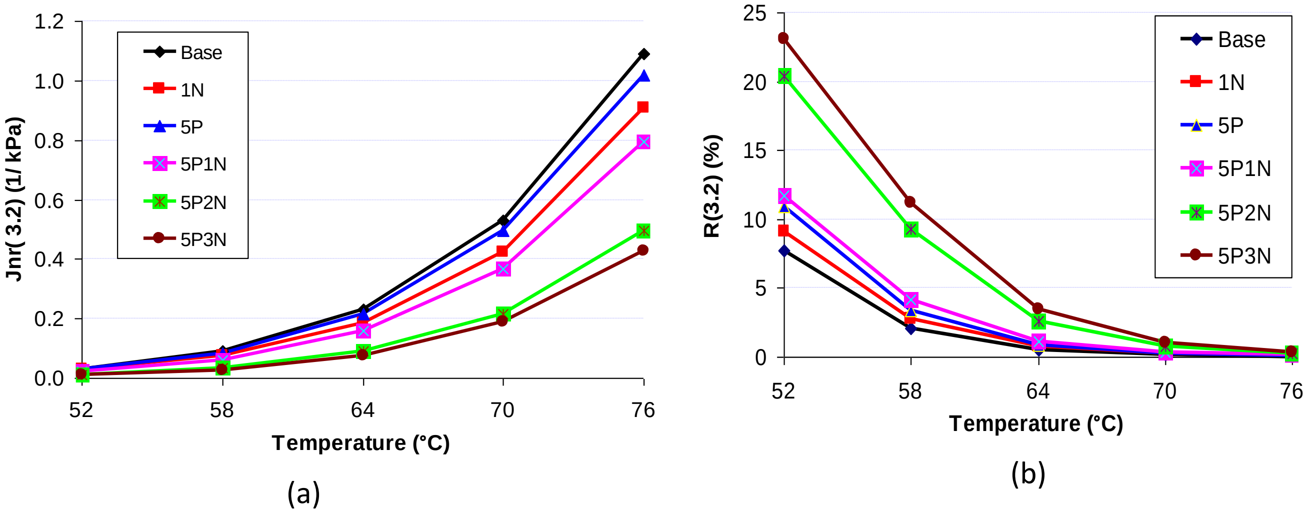


Figure 8. MSCR parameters at different temperature

(a) average non-recoverable creep compliance (J_{nr}) at 3.2 kPa;

(b) average percent recovery (R) at 3.2 kPa

3.6. Aging sensitivity analysis

The PAR, SPI, and VAI of modified asphalt and unmodified asphalt are shown in Table 4. It is clear that the PAR value was increased when adding PVC, NS, and PN. The PAR value of virgin asphalt was increased by 27.09%, 54.16%, and 59.49% when added 1%NS, 5%PVC, and 5% of PVC with 1% NS, respectively. The asphalt binder modified was the highest value of PAR with 5P3N. The higher the PAR values meaning that the higher the degree of resistance to aging.

The SPI values reduce with an increment of the PVC and NS concentration. Base asphalt AH#70 had the highest value of SPI, and asphalt binder modified with 5P2N was the lowest value of SPI. Adding PN was also lower value of SPI than adding only PVC or NS and virgin asphalt. The higher SPI value can be indicated for large changes in high rising temperature individual after short-term aging progress.

The VAI value of the virgin binder was decreased by 19.07%, 48.51%, and 79.05% when used 1%NS, 5%PVC and 5P1N. The virgin asphalt of VAI value is higher than all types of modified asphalt. The lower VAI value of asphalt indicate the stronger anti-aging capacity of asphalt binder.

Through PAR, SPI, and VAI is confirmed that using PVC, NS, and PN enhanced the aging resistance of the asphalt binder.

Table 4. Aging sensitivity with difference index

Binder	Aging indices at difference index		
	PAR (%)	SPI (C)	VAI @135 (%)
Base	44.77	7.15	64.90
1N	56.90	5.50	52.52
5P	75.59	3.50	39.42
5P1N	89.74	2.50	33.74
5P2N	92.09	1.20	23.77
5P3N	96.76	1.70	37.28

The AIR values measured for the NS, PVC and PN modified binder at different temperatures are shown in Table 5, which displays that the AI of each binder kind is higher than 1, and the processing RTFO made asphalt binder became harder. The AIR value rise observed after aging is caused by the rise in the complex modulus.

Table 5. AIR values estimated for various asphalt binders at different temperatures

Binder	Aging indices at difference temperatures				
	52^{0}C	**58^{0}C**	**64^{0}C**	**70^{0}C**	**76^{0}C**
Base	2.44	2.47	2.38	2.28	2.15
1N	2.53	2.48	2.35	2.20	2.10
5P	2.66	2.88	3.04	3.10	3.11
5P1N	2.46	2.60	2.70	2.75	2.74
5P2N	2.15	2.23	2.29	2.32	2.30
5P3N	2.08	2.12	2.14	2.16	2.16

4. CONCLUSION

Based on the results obtained, the following conclusions are drawn from this research:

1. The value of penetration decreased with rising PVC, NS, and PN contents. On the contrary, the value of the softening point increased, proving that an asphalt binder modified with PVC, NS, and PN can resist deformation under high temperatures.

2. The measured $G^*/\sin(\delta)$ values and δ values decreased with the addition of PVC and NS, enhancing the elastic response of the binder and permanent deformation resistance. Results show that the modified asphalt may be appropriate for high-temperature service pavements.

3. From the MSCR parameters, it is clear that PN-modified asphalt has the highest resistance to rutting, performing better under high temperatures than PVC- modified or NS-modified asphalt.

4. Through the short-term aging RTFO test, PVC and NS had useful effects on the anti-aging of the asphalt binder, the combination of PVC and NS had better short-term aging resistance than only adding PVC or NS.

Conflict of interest

No conflict of interest was reported by the authors.

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