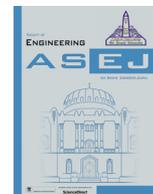




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## Chemical and physical properties of poly (lactic) acid modified bitumen

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## ABSTRACT

This study investigates the feasibility and effect of poly(lactic) acid (PLA) on bitumen modification. The chemical and physical properties were evaluated for the modified bitumen produced with varying percentages of PLA ranging from 3 to 9%. Several testings such as the nuclear magnetic resonance (NMR), Fourier Transform Infrared Spectroscopy (FTIR), Gel permeation chromatography (GPC), penetration, softening and ductility, and thermal storage stability were evaluated. The results show that chemical interaction exists between PLA and bitumen. The GPC analysis indicates high compatibility of the bitumen with the PLA modifier. Moreover, the results indicated that the addition of PLA increased the consistency of modified bitumen. The storage stability and segregation of phases were positively affected in the PLA modified bitumen. The PLA and base bitumen interact at physical and chemical levels which results in enhancement of performance of modified bitumen to produce a high-quality binding material for pavement construction.

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## 1. Introduction

Bitumen is produced by refining crude oil through a series of distillation processes and it is composed of heavy hydrocarbons, which are classified into saturates, aromatics, resins and asphaltenes [1]. It is used in various engineering applications such as highway and airfield pavement due to its physical and rheological characteristics as well as impermeability and adhesive properties [2,3]. However, being a viscoelastic material, bitumen is easily affected by seasonal temperature and rain as well as loading factors including increasing traffic volumes and continuous heavy loads [4–6]. The viscoelastic properties of bitumen are time and temperature dependant. This effect changes in its physical properties, which are reflected in the mechanical properties of asphalt mixtures. Therefore, bitumen should be sufficiently stiff to resist

rutting at high temperatures and soft at low temperatures to prevent the occurrence of thermal cracking [7,8].

The performance bitumen is, traditionally, enhanced with different types of modifiers including; nanomaterial [9,10], geopolymer [4,11–13], waste materials such as glass and plastic [14], and rubber [15]. The previous studies indicate that the addition of modifier improves the performance of the binder in terms of elasticity and stiffness, and also reduces the permanent deformation of the pavement resulting from environmental effects and repetitive traffic loading [16–18]). However, amongst the different types of bitumen modifiers, the polymers are the frequently used as modifiers and have demonstrated to be good modifying agents in the production of high-performance binder [17,19–22].

The evidence for performance enhancement with polymers is demonstrated by Jiang et al. [23] and Laukkanen et al. [24]. According to the studies, the modification of bitumen with SBS enhances the engineering properties of the bitumen for reduced temperature dependence, increased elasticity, as well as an enhanced performance at low and high service temperature. This is due to the excellent mechanical properties of SBS such as high fatigue resistance, elastic recovery and high resistance at extreme temperatures [25–27]. Another thermoplastic modifier that has been widely used for bitumen modification is crumb rubber (CR). According to Poovaneshvaran et al. [28], Wang et al. [29–31] and

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Yao et al. [32] CR can modify the physical and mechanical properties of bitumen to produce improved resistance to fatigue and thermal cracking, ageing, and rutting. Loderer et al. [33] reported that, unlike SBS-modified bitumen, CR-modified bitumen has a high resistance to rutting and low-temperature cracking. Moreover, other studies on bitumen modification with natural rubber show enhancement of physical and rheological properties of the modified bitumen [34] and improvement in resistance to shear stress [28]. Furthermore, the modification of bitumen with polymers has demonstrated to improve the binder properties, for instance, enhanced stiffness at high temperatures, cracking resistance at low temperatures, moisture resistance, and longer fatigue life ([15,35,36]. The promising potential of using polymers such as rubber and geopolymer is not limited to the bituminous materials only. Numerous evidences were found related to the promising effect of using these polymers in other applications including as structural and concrete materials [37,38].

The findings of the previous studies related to the polymer modified bitumen are promising and establish the applicability of polymer in bitumen. Within this scope, this research explores the potential of PLA as a modifier. PLA is a bio-based green thermoplastic polyester which can be derived from renewable resources such as sugarcane or cornstarch [39,40]. Furthermore, PLA is an attractive substitute for conventional polymers due to its excellent biocompatibility, high tensile strength, and high modulus. The simplicity of the PLA structure with esters as the repeating unit and carboxyl group as the end chain can explain the chemical reaction that occurs between PLA and bitumen.

The pavement engineering field, traditionally, has remained less focused on the chemical reaction occurring between the polymers and bitumen. Since the past several years, the major concern in literature is enhancing the stability and compatibility of bitumen-polymer blends and optimizing the formulation of the blends [29]. Most reported works on the utilization of polymers as a modifier focus on describing the physical dispersion of polymers in bitumen while ignoring the chemical reaction that occurs in the blend [12,41].

In view of the limitations of previous works, this study aims to investigate the chemical and physical performance of modified bitumen with a new bitumen modifier known as poly(lactic acid) (PLA). This research examines the chemical interaction occurring between the PLA and the base bitumen by using multiple spectroscopic techniques. The relationship of the interactions is then confirmed using the sequential dissolution approach, where a reaction mechanism between PLA and bitumen is also proposed. The PLA-bitumen compatibility and the dispersion of PLA in bitumen are also discussed. The current study will be useful to understand the behaviour and properties of PLA in bitumen modification for its potential utilization in pavement engineering. The remainder of this paper is structured as follows. Section 2 describes the materials, blending and testing protocol. Section 3 presents the results and discussion of the outcome in this study. The paper ends with conclusion and recommendations for future research in Section 4.

## 2. Material and methods

### 2.1. Materials

Poly(lactic acid) (PLA) in pellet form with a melt flow index (MFI) of 20 g/10 min (190 °C/2.16 kg) and a density of 1.24 g/cm<sup>3</sup> was purchased from Shenzhen Bright China Industrial Co, while the chloroform was obtained from Merck Pvt Ltd, Selangor, Malaysia. The filter paper (Whatman, 150 mm, Catalog Number 1001–150) was purchased from a local supplier, and the 60/70 penetration grade bitumen was supplied by a refinery in Port

Klang, Malaysia. The physical properties of the 60/70 penetration grade bitumen used in this study are presented in Table 1.

### 2.2. Preparation of bitumen blends

Aluminum cans (500 cm<sup>3</sup>) were filled with 200 g of 60/70 penetration grade bitumen and put in a 150 °C oven until they are ready for use. The PLA was dissolved in an appropriate volume of chloroform to obtain a final concentration of 3, 5, 7 and 9 wt% by base bitumen (250 g). The semi-liquid PLA was gradually added (2 mL/min) to the base bitumen at 180 ± 2 °C and a high-shear mixer to blend at 1000 ± 10 rpm for two hours to obtain a homogeneous mixture. After this step, the mixture was aliquoted into different cans for subsequent physical and chemical testing. The experimental process of the development of PLA modified bitumen is presented in Fig. 1.

## 3. Characterization of reactive polymer with bitumen

Proton (<sup>1</sup>H)-nuclear magnetic resonance (NMR) spectra was used to study the structural distribution of PLA and their interaction with the bitumen. The analysis was carried out using the Bruker Advance III HD 400 MHz 1-Dimensional NMR spectroscopy with tetramethylsilane (TMS) as the internal standard. Each sample was dissolved in deuterated chloroform (CDCl<sub>3</sub>) to a final concentration of 10% w/v and the run time was 10 min. Fourier-Transform Infrared spectroscopy (FT-IR) was carried out to determine the functional groups and the chemical bonds in the PLA-modified bitumen. All samples were tested in triplicate using the Perkin Elmer Spectrum 400-FT-IR spectrometer.

The compatibility of PLA with base bitumen was determined by analyzing the asphaltene using sequential dissolution via staged extraction approach. The 100 mg samples of bitumen and modified bitumen with 3, 5, 7 and 9% PLA, were washed three times with 10 mL of chloroform. Each layer was then filtered with using a filter paper. The residue (in the form of asphaltene) retained on the filter paper was weighed and compared with the control bitumen. Next, the extracted asphaltene from the third wash of each sample were recovered and characterized using FT-IR spectroscopy.

Gel permeation chromatography (GPC) was employed to analyze the dispersity of PLA in the base bitumen. Dispersity was determined based on molar mass and molar-mass distribution of the polymer obtained from GPC (Waters 1515) equipped with differential refractive index (RI 2410) and ultraviolet (UV 2487) detectors. The molar masses were separated using Waters Styragel columns in a series with the molar mass ranging from 100 to 500 000 gmol<sup>-1</sup>. The samples were dissolved in chloroform and analyzed using tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min (30 °C) for 40 min.

## 4. Characterization of PLA-modified bitumen

The physical characterization of PLA-modified bitumen includes performing the penetration test at a fixed temperature (25 °C) according to ASTM D5 [42] while the softening point was

**Table 1**  
Physical properties of 60/70 penetration grade bitumen.

Parameter	Standard	Unit	Specification
Penetration at 25 °C	ASTM D5	mm/10	60/70
Softening point	ASTM D36	°C	49/56
Ductility at 25 °C	ASTM D113	cm	100 min
Loss of heating	ASTM D6	wt. %	0.2 max
Drop in penetration after heating	ASTM D5-D6	%	20 max

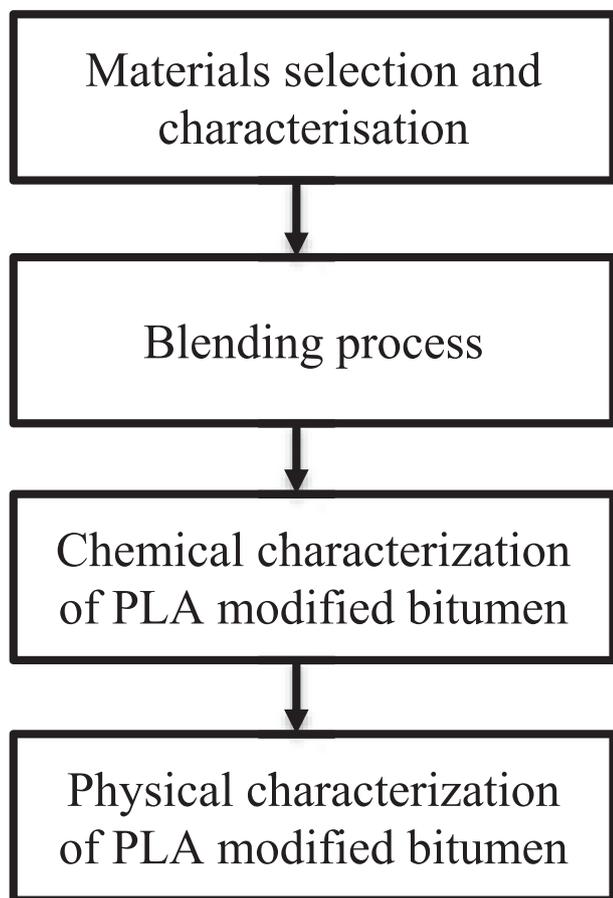


Fig. 1. Research methodology.

measured with ring and ball approach as per ASTM D36-06 [43] standard. The stability test was carried out by placing the bitumen in an aluminum-covered tube with a diameter of 3.5 cm and a height of 30 cm in a 180 °C oven for three days. The samples were then cooled at ambient temperature and then cut into three sections. The upper and lower sections of each sample were subjected to softening temperature test. The degree of homogeneity of the mixture is indicated by differences in softening temperature between the two sections, where a smaller difference indicates high compatibility of the PLA with bitumen. The ductility test was carried out according to ASTM D113 [44] standard at 25 °C.

## 5. Results and discussion

### 5.1. Characterization of PLA-bitumen reaction

#### 5.1.1. 1-Dimensional nucleus magnetic resonance proton ( $^1\text{H}$ 1D-NMR) analysis

In order to demonstrate the interaction between PLA and bitumen, a representative  $^1\text{H}$  NMR spectrums and the assigned signals of the control and the bitumen modified with varying percentages of PLA (Figs. 2–4). The results in Fig. 2 show that there are multiple signals from the chemical shift from 0.8 to 3.5 ppm. The signals were assigned as two parts, the part 'a' ranges from 0.8 to 1.4 ppm and represents the signals of the aliphatic proton from alkanes. The 'b' ranges from 1.5 to 3.5 ppm and represents the protons from alkenes, alkynes or aliphatic with carbonyl such as ketone, aldehyde, ester and carboxyl group. The chemical structure for poly(lactic acid) is shown in Fig. 3, where two signals have been detected. The doublet peak absorbed at a chemical shift from 1.58

to 1.60 ppm (labelled c) indicates a proton from methyl group ( $-\text{CH}_3$ ), and the quartet peak at 5.15–5.20 ppm (labelled d) indicates a proton from the ester side chain ( $-\text{OCH}(\text{CH}_3)-$ ) of the repeating unit of PLA. Fig. 4 shows the stacked NMR of the bitumen modified with 3, 5, 7 and 9% PLA. The four detected signals (a, b, c and d) indicate the occurrence of a chemical interaction between the PLA and the bitumen. The increase in the intensity of the doublet and quartet (peaks c and d) corresponds with the high percentage of PLA in the samples. A comparison with the control bitumen shows the suppression of the signals in the 'b' region (Fig. 4B) of the PLA-modified bitumen.

#### 5.1.2. Fourier-Transform Infrared (FT-IR) analysis

Fig. 5 shows a comparison of the FT-IR spectrum of the control bitumen, PLA and the bitumen modified with 3, 5, 7 and 9% PLA. The spectrum shows that the bitumen modified with different percentages of PLA have similar overlapping profiles. A comparison of the spectrum for samples modified with PLA with control bitumen and PLA shows an almost similar profile except for the additional bands at 1098  $\text{cm}^{-1}$  (region i) and 1749  $\text{cm}^{-1}$  (region ii) in the modified bitumen. This indicates the simultaneous presence of the carbon-oxygen (C-O) and carbonyl (C = O) functional groups. A comparison with the PLA spectrum shows a decreased transmittance percentage in the PLA-modified bitumen in region iii (3600–3650  $\text{cm}^{-1}$ ) for the band representing the hydroxyl group (OH).

The compatibility of PLA with bitumen was investigated using sequential dissolution technique via the staged extraction method. The asphaltenes from each sample (the third wash) were extracted and sent for FT-IR analysis to determine their carbonyl index. Fig. 6 shows the percentage of asphaltenes for bitumen modified with 3, 5, 7 and 9% PLA. The results are comparable with the percentage of the control bitumen (~14.4%), except for higher asphaltenes content observed in the bitumen modified with 9% PLA (18.1%). Based on the FT-IR spectrum, the carbonyl index (CI) was determined by calculating the area under the carbonyl band absorbed at wavelength 1695  $\text{cm}^{-1}$  and the saturated C-C band at 1455  $\text{cm}^{-1}$  (Eq. (1)). The same asphaltenes residue shows that the carbonyl index of the bitumen modified with 3, 5 and 7% PLA are slightly higher (~16.3%) than that of the control bitumen (14.5%). Similar to the asphaltenes content, bitumen modified with 9% PLA has a high carbonyl index of 19.7% (Fig. 6).

$$\text{CI} = \frac{\text{area of carbonyl at } 1695 \text{ cm}^{-1}}{\text{area of saturated C - C at } 1455 \text{ cm}^{-1}} \times 100 \quad (1)$$

The FT-IR spectrum presented in Fig. 5 and the sequential dissolution technique were used as a basis for further investigation of the correlation between the additional C-O band at 1098  $\text{cm}^{-1}$  (region i) and C = O band at 1749  $\text{cm}^{-1}$  (region ii) in the PLA-modified bitumen. The spectrum in Fig. 5 which were PLA-modified bitumen was labelled as unwashed (UW) and the PLA-modified bitumen that underwent sequential dissolution notated as washed samples sequential dissolution (WSD). The results were compared to understand the interaction between the PLA and the bitumen. Fig. 7 shows the percentage index of C-O bond (region i) while Fig. 8 shows the result of C = O (region ii) divided with the area of (A) unsaturated C = C at 1650  $\text{cm}^{-1}$  and (B) saturated C-C at 1455  $\text{cm}^{-1}$ . The index pattern of the C-O bond is observed to be different from that of C = O when divided with the unsaturated and saturated carbon-carbon interaction. Fig. 7 indicates that the UW showed a simultaneous increase from control bitumen in the index of C-O and C = O with C = C from 11.0 to 26.3% and 4.7 to 17.9% respectively and C = O with C-C index from 1.0 to 7.3%. While a decreasing pattern of UW sample for C-O bond with C-C index from 11.0 to 7.0% observed. On the other hand, for WSD samples, the

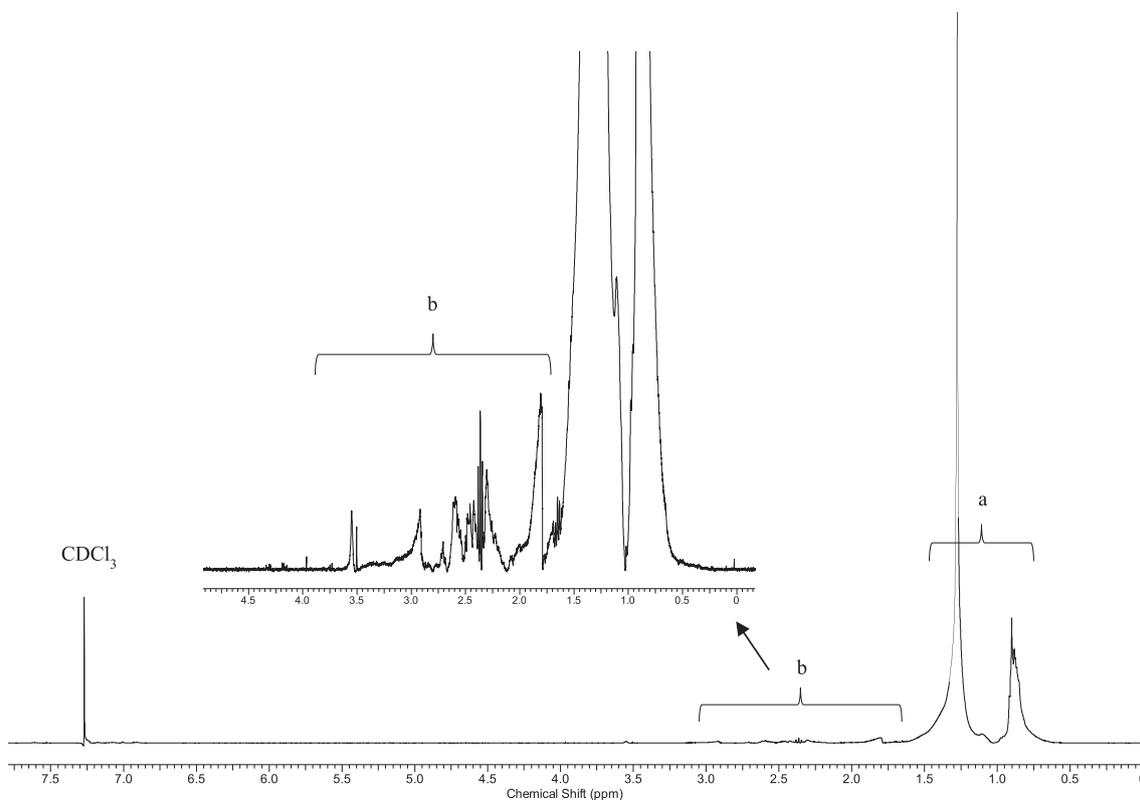


Fig. 2. <sup>1</sup>H NMR spectrum of control bitumen.

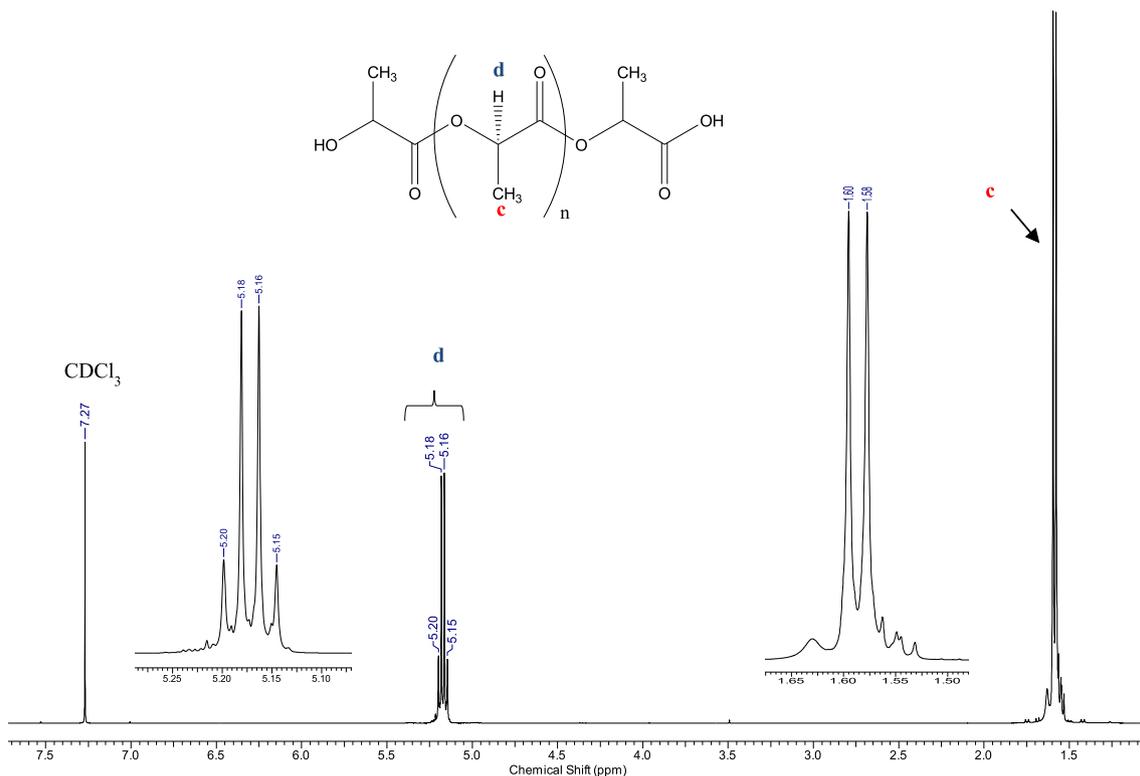


Fig. 3. <sup>1</sup>H NMR spectrum of PLA.

result did not show any significant difference in the index of C-O with C = C (~11.1%) except for the 9% PLA (12.7%). Together with UW samples, WSD also showed a decreasing index pattern of

C-O bond with C-C from 10.6 to 5.1%. However, an increasing indexes pattern showed for WSD samples of C = O with C = C and C-C each from 12.1 to 16.9% and 9.0 to 18.9% respectively.

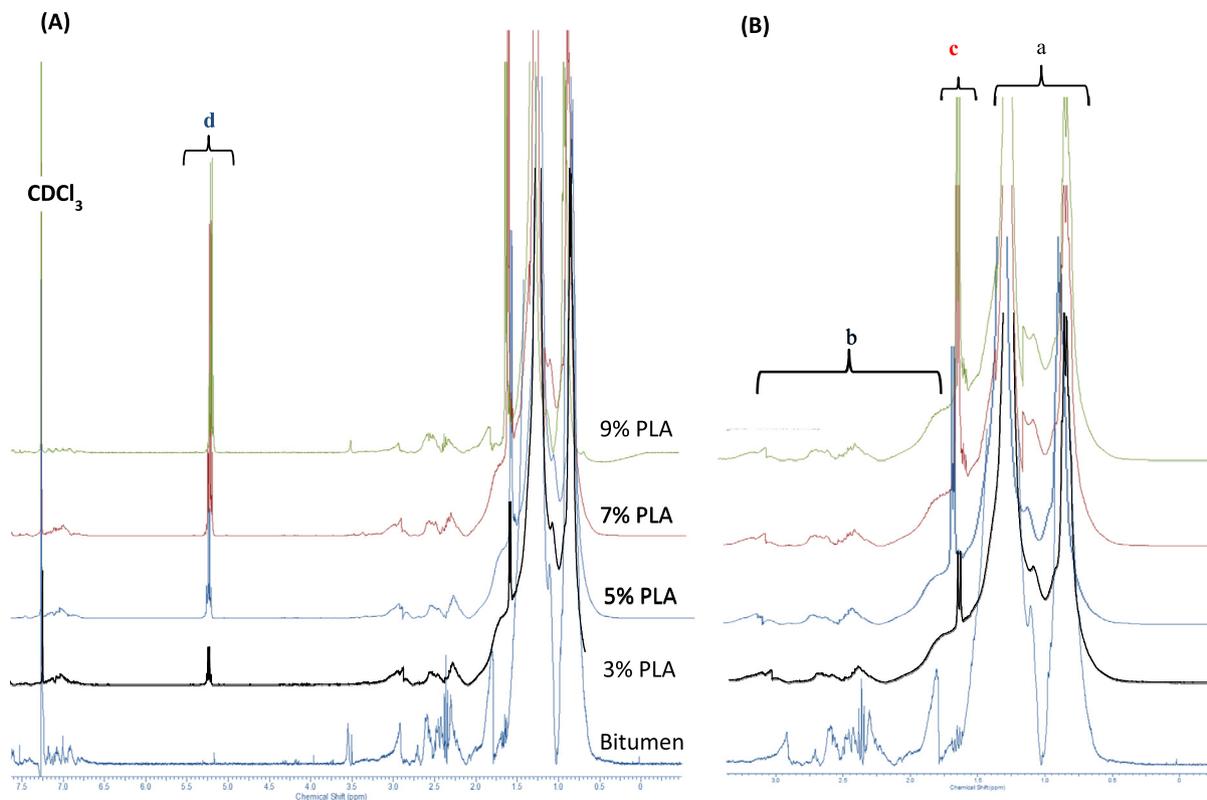


Fig. 4. (A) <sup>1</sup>H NMR spectrum of the bitumen modified with 3, 5, 7 and 9% PLA. (B) Zoom <sup>1</sup>H NMR spectrum between 0.5 and 3.0 ppm of the bitumen modified with 3, 5, 7 and 9% PLA.

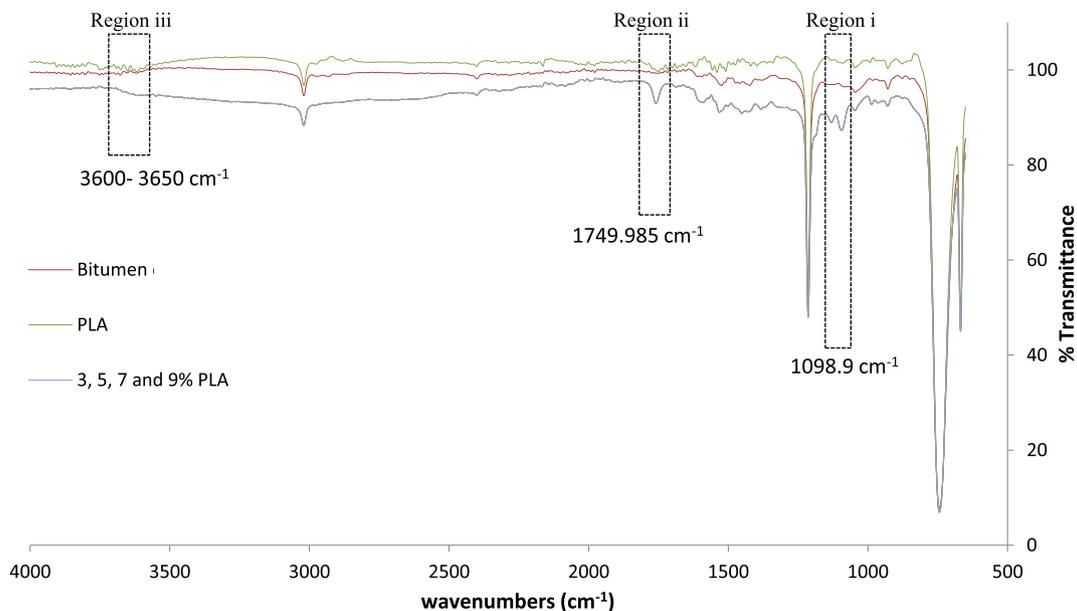


Fig. 5. FT-IR spectrum of the control bitumen, PLA and bitumen modified with 3, 5, 7 and 9% PLA.

5.1.3. Gel permeation chromatography (GPC) analysis

The molar mass and molar-mass distribution or dispersity of PLA throughout the bitumen were examined using GPC. Fig. 9 is the stacked GPC chromatograms of the control bitumen and the PLA-modified bitumen, while Fig. 10 shows the zoom chromatograms of the distribution and dispersity of PLA in bitumen. Two peaks can be seen in the control bitumen sample eluted at retention times of 25.0 and 30.3 min. The two major peaks repre-

sent bitumen and are present in all PLA-modified bitumen samples (Fig. 9). However, Fig. 10 shows that, when PLA is added to the bitumen, the increase in the numbers of peaks correspond with the increasing percentage of PLA (from 3, 5, 7 to 9% PLA). The distribution of PLA peaks at a retention time of 25 min varies between samples while the major peak (at 30.3 mins) is not affected. The large fragments of PLA peaks eluted at retention time 25 min indicate the poly-dispersity of PLA within the samples. Thus, the prop-

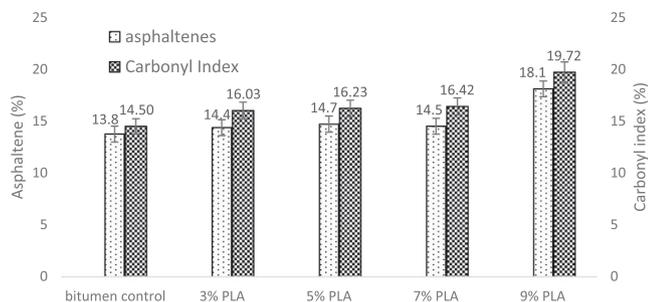


Fig. 6. Compatibility and sequential dissolution of different percentages of PLA and bitumen.

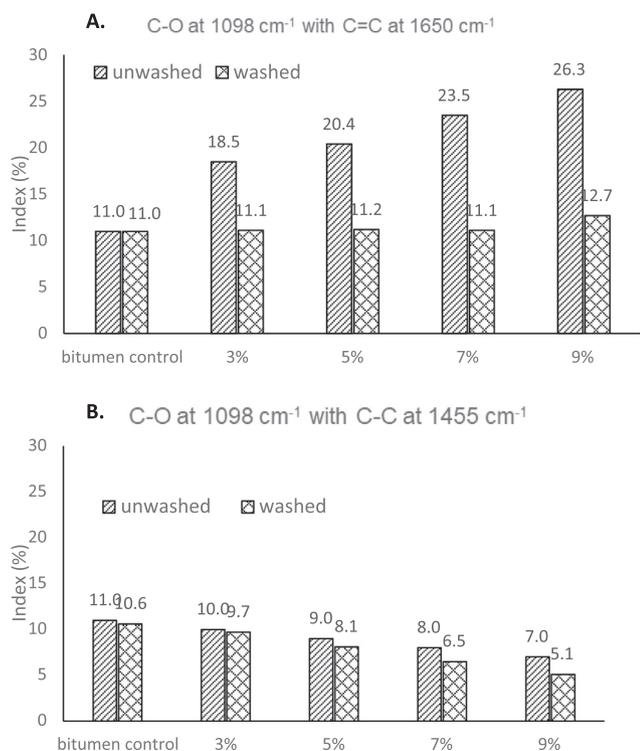


Fig. 7. Comparison of washed and unwashed indexes of C-O bond at 1749 cm⁻¹ (region i) with (A) C = C, and (B) C-C bonds using FT-IR analysis.

erties of all peaks at the 25.0-minute retention time were further investigated and the results are shown in Table 2. The table shows that the retention time of the second major peak in all samples shifted about ± 0.1 min, the effect of the size of exclusion column separation. The values of peak molecular weight, average molecular weight, average molar mass and molar distribution (dispersity) increased with PLA modification (Table 2). The varying dispersity for the 3 and 5% (1.089 and 1.136) and the 7 and 9% (1.653 and 1.984) bitumen-PLA indicate that the dispersity of PLA is enhanced when 7% and 9% of PLA were added to the bitumen.

### 5.2. Performance of PLA-modified bitumen

The effect of PLA on the properties of modified bitumen was evaluated based on the physical performance including; penetration, softening point, ductility and storage stability. Fig. 11 presents the result of the penetration values of the binders. The penetration is an indication of bitumen consistency, which is an empirical measure of the resistance of bitumen to continuous deformation. The addition of PLA to bitumen changes the penetration value of the

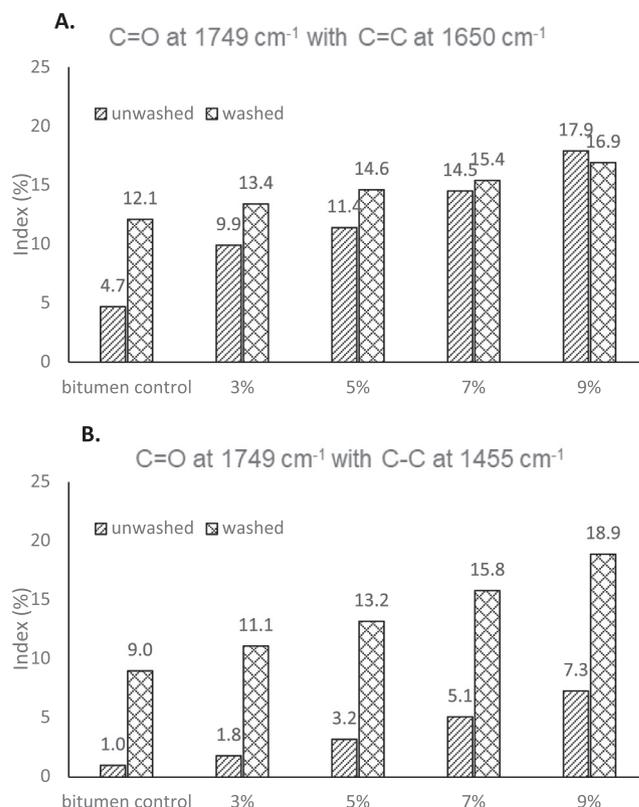


Fig. 8. Comparison of washed and unwashed indexes of carbonyl at 1749 cm⁻¹ (region ii) with (A) C = C, and (B) C-C bonds using FT-IR analysis.

binders (Fig. 11). The bitumen added with more quantity of PLA (7% and 9%) shows low penetration values as compared to the base bitumen. This indicates the ability of the PLA modifier to enhance bitumen stiffness. The penetration result shows a peculiar trend, where the addition of 3% of PLA increases the penetration value up to 18.5% in comparison to the base bitumen, after which penetration gradually decreases with high PLA content. This is due to the dispersion level of PLA in bitumen. Based on dispersity reported earlier, the dispersity of 3% PLA in bitumen is low, and this has the effect of softening the binder. The gradual decrease of the value observed with the addition of high amounts of PLA (5% to 9%) is due to the high dispersity of PLA in bitumen. Furthermore, the high fatigue resistance and elastic recovery of PLA are similar to other thermoplastic materials such as SBS, crumb rubber and natural rubber and contribute to the improvement of bitumen's consistency [25–28,32]. High amounts of PLA in bitumen results in improved mechanical properties (from PLA) of the modified bitumen, and as a result increases the stiffness of the binder. This increase may also be due to the enhanced structural chain mobility properties of the modified bitumen.

The softening point value of PLA-modified bitumen (Fig. 12) is directly proportional to the amount of PLA in bitumen. The high PLA content in bitumen increased the asphaltene ratio in modified binders and this contributes to improving the stiffening properties of modified bitumen. As a result, it reduces the susceptibility of the modified binder to temperature changes. The less susceptibility of bitumen such as PLA modified bitumen indicated the high performance of bitumen at high temperature [14,15]. This is congruent with the observation made by Poovaneshvaran et al. [28], Rosyidi et al. [12] and Yusoff et al., [10] about the ability of modified bitumen to withstand high temperatures as compared to base bitumen. In addition, the ductility value of PLA-modified bitumen is > 100 cm, which is similar to the value for the base bitumen

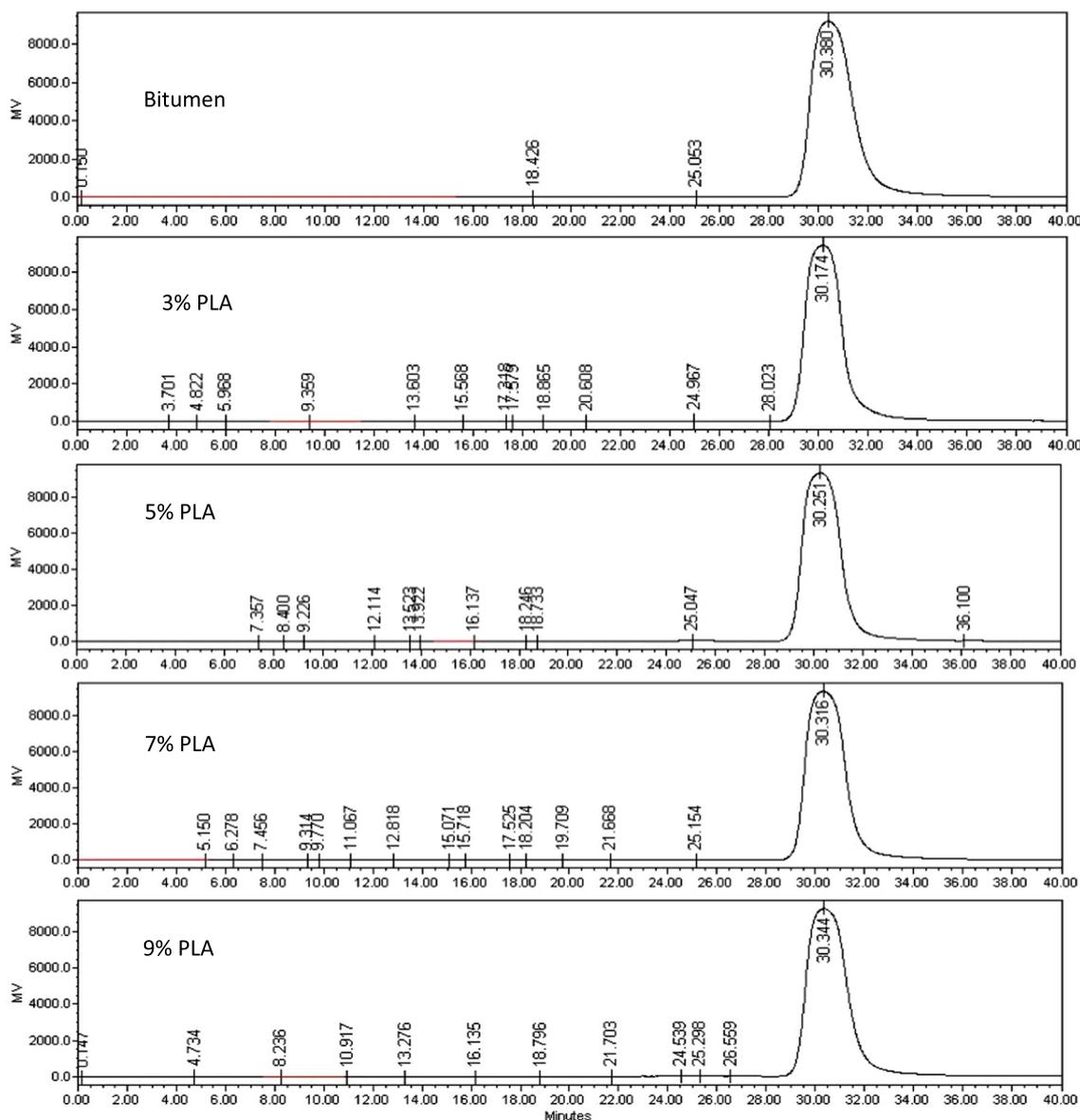


Fig. 9. Gel permeable chromatography (GPC) of the control and modified bitumen.

(See Table 3). The physical properties of PLA-modified bitumen reported in this study are comparable with those reported in earlier studies, including Al-Mansob et al. [15], Ibrahim et al. [4], Poovaneshvaran et al. [28] and Ali et al. [11].

On the other hand, the main concern with polymer modified bitumen is the storage stability of the modified bitumen. According to Yu et al. [45], the modified bitumen is considered stable when the difference between the softening point of the upper and lower sections of the samples after storage under certain condition is less than 2.5 °C. The difference in softening points of the top and bottom sections of the samples determines the degree of phase separation. During high-temperature storage, the phase separation occurs when the modifier is not dissolved in the modified bitumen and result in the non-homogeneous mixture. Hosseinezhad et al. [46] argued that the occurrence of phase separation is influenced by the solubility and particle size of the modifier and density of both the modifier and bitumen. According to the literature, polymer-modified bitumen with poor storage stability is not suitable for paving, roofing, and industrial specialty product applications [47–49].

Bitumen modified with functionalized polymers, such as PLA, have high thermal stability and no phase separation. This is indicated by the small temperature difference (less than 2.5 °C) between the top and bottom sections of the sample, except for the bitumen modified with 9% PLA (See Table 3). The poor thermal storage stability of the bitumen modified with 9% PLA is due to the less compatibility between PLA and bitumen.

### 5.3. Discussion of the results

In this study, polymer modification of bitumen involves the physical blending of the polymer with bitumen as well as the chemical reactions between the two materials as recommended by Brasileiro et al., [17] and Cardone et al., [50]. Nuclear magnetic resonance (NMR) is a spectroscopic method that can provide information about the number of magnetically distinct atoms such as hydrogen nuclei (protons). NMR differs from Infrared (IR) related to the approach of NMR reveals the type of functional groups present in a molecule. By combining the utilization of NMR and IR spectroscopies, this study is able to gather sufficient evidence on

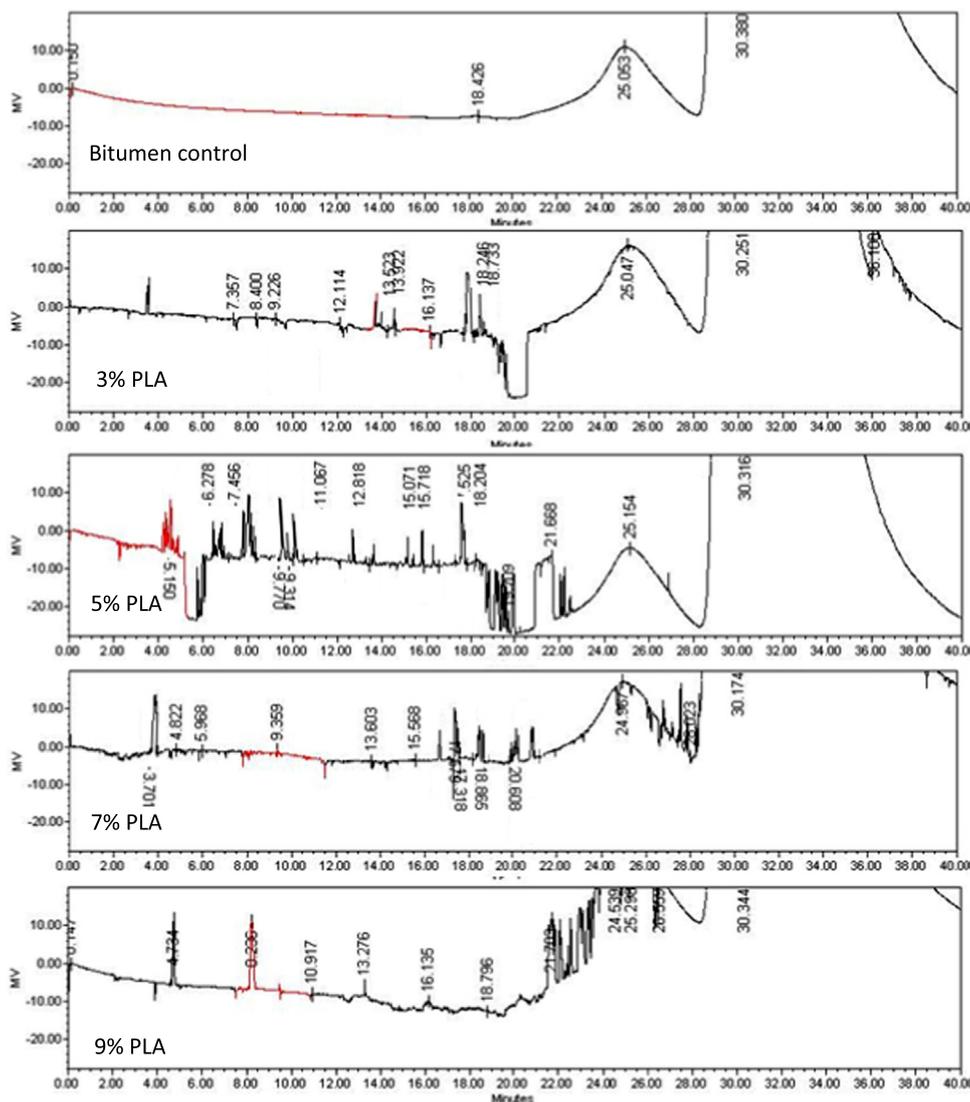


Fig. 10. Zoom GPC of the control and modified bitumen.

Table 2  
Molecular properties of bitumen modified with PLA.

Sample	Retention time (min)	Peak Molecular Weight (MP)	Average Molecular Weight (Mw)	Average molar mass (Mn)	Dispersity (Mw/Mn)
Control Sample	25.063	1633	1253	1205	1.039
3% PLA	25.047	1659	1331	1222	1.089
5% PLA	25.154	1701	1456	1281	1.136
7% PLA	25.157	1786	2161	1307	1.653
9% PLA	25.134	1805	2749	1385	1.984

the chemical interactions between the bitumen and poly(lactic acid) (PLA). In NMR analysis, different types of protons (H) are represented as peak signals in the spectrum having different chemical shifts. The NMR of the control bitumen (Fig. 2) shows that signals are absorbed at a different range of chemical shift. The signals from 0.8 to 1.4 ppm in the region (a) represent the protons from aliphatic alkanes. It can be concluded that most of the protons in the base bitumen are alkanes, whether they are from the primary (R-CH<sub>3</sub>), secondary (R-CH<sub>2</sub>-R) or tertiary alkanes (R<sub>3</sub>CH). The two singlet peaks in this region indicate that these protons are bonded with other functional groups (R), for instance, oxygen. The signals in the region (b) are protons which represent alkenes, alkynes, aliphatic carbonyl functional group or protons bonded with phenyl (aro-

matic as side chain). In addition, no other signals are observed in the spectrums. This indicated the occurrence of other chemical shift (between 6.5 and 8.0 ppm) which represented the aromatic protons. However, it is known that bitumen contains a lot of aromatic compounds [51], thus, it can be deduced that the aromatic group in the bitumen is present as the phenyl group and no free protons are attached at the aromatic structure.

The NMR spectrum of PLA (Fig. 3) shows two signals, where one of the peaks is a doublet, indicating the protons from the methyl group (assigned as c), and the second peak is a quartet, which indicates the proton assigned as (d). Proton (d) is more shielded (appears at a high chemical shift) compared to the methyl group and more electronegative when interacting closely with two oxy-

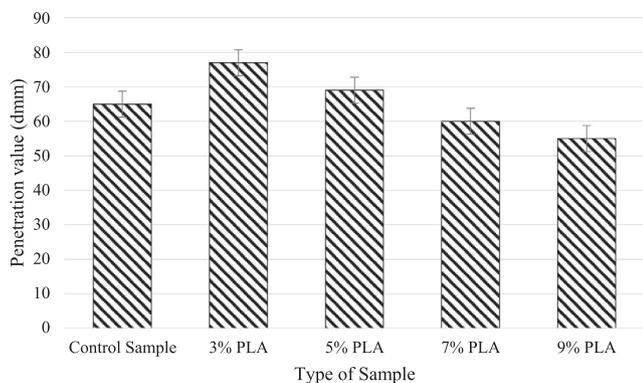


Fig. 11. Penetration values at 25 °C.

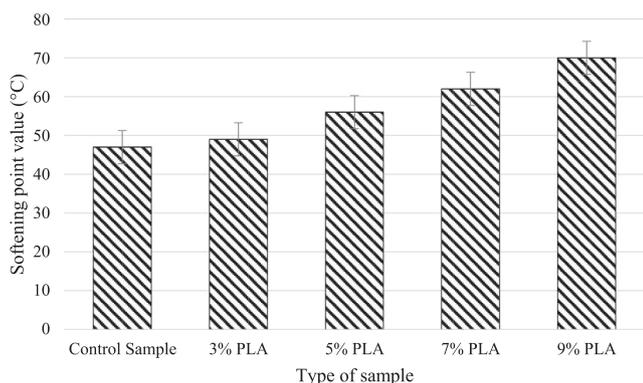


Fig. 12. Softening point values.

gen atoms next to each other. The results of NMR analysis of the bitumen modified with 3, 5, 7 and 9% PLA (Fig. 4) show that all signals from the bitumen and PLA (a, b, c, and d) appear at each chemical shift. The increase in the observed intensity of the signals for PLA corresponds with the increasing concentration of PLA in the samples. However, the signals in the region (b) of the modified samples seem to be suppressed. The suppression of the signals in this area indicates the loss of the proton absorbed at this chemical shift. This is because one of the functional groups (either carbonyl groups or aliphatic alkenes/alkynes) from this region interacts with PLA; this is later confirmed by the result of the FT-IR analysis.

FT-IR analysis of the base bitumen, PLA and PLA modified bitumen (Fig. 5) show two additional bands at wavenumbers 1098.9 (region i) and 1749.9 cm<sup>-1</sup> (region ii) and the PLA-modified bitumen show a decrease in a band at 3600–3650 cm<sup>-1</sup> relative to PLA. The new functional groups in the PLA-modified bitumen sample (carbon–oxygen bonding (C–O) in region i and carbonyl group (C = O) in region ii) support the result of NMR analysis. The occurrence of new functional groups in the PLA-modified bitumen represented the PLA is compatible with the base bitumen. The PLA and bitumen are chemically interacting with the base bitumen during blending. The disappearance of the band in region iii, repre-

sented by the hydroxyl group (OH), shows the reaction between the base bitumen and PLA occurring at the OH group; this has resulted in the formation of new C–O and C = O bonding. However, the result is not sufficient for predicting the functional group in the base bitumen reacting with the OH group of the PLA. Thus, sequential dissolution was carried out to determine the compatibility of PLA with the bitumen.

The approach for investigating sequential dissolution was formulated by Corbett [52] and has been utilized by many researchers. Sequential dissolution is carried out to evaluate the oxidation process that occurs between the binder and the bitumen. Generally, there is a net reduction of maltenes fraction during an oxidation reaction, which occurs simultaneously with an increase in asphaltene fraction. The formation of carbonyl functionalities within the binder is linked with the increase in asphaltene during a sequential dissolution. Thus, an increase in carbonyl functionalities is anticipated during the later stages of the extraction process when a binder is being sequentially dissolved. In this study, sequential dissolution was used to investigate the compatibility of PLA as a modifier for bitumen, thereby determining the interaction of asphaltene with PLA. All samples (base bitumen and bitumen modified with 3, 5, 7 and 9% PLA) were washed with the same volume of chloroform (w/v). The result presented in Fig. 6 shows that the standard deviation does not exceed 1. The fractionation of the bitumen modified with 3, 5 and 7% PLA with chloroform yielded 14.4 ± 0.8% asphaltenes, slightly higher than the amount produced by the control bitumen (13.8 ± 0.2%). The lack of significant difference in the value indicates absence of sequential dissolution and PLA in concentrations of 3, 5 and 7% are compatible with the base bitumen.

The bitumen modified with 9% PLA show a ± 5% change in asphaltene content in comparison to the control sample, indicating the compatibility of PLA with bitumen base does not exceed 7%. A sufficient degree of polymer–bitumen compatibility is required to prevent separation during storage, pumping and application of the asphalt mixture, as well as to ensure required properties for pavements. Polymer modified bitumen with poor storage stability is not suitable for applications such as paving binder, roofing, and other industrial speciality products [47–49]. The results of NMR and FTIR are supported by the carbonyl index shown in Fig. 6, where the carbonyl index is directly proportional to the release of asphaltenes. It should be noted that the solvent used in this study, i.e. chloroform, has never been reported to be one of the solvents with good compatibility with bitumen. The amount of asphaltenes released due to the utilization of chloroform (13.8 ± 0.2%) is lower than most of the solvents tested, such as TCE (16.7%), THF (22.5%), toluene (19.7%) and decalin (22.6%) [53]. The low percentage of asphaltenes released by chloroform is an indication of its high solubility.

FT-IR analysis of sequential dissolution was carried out to further investigate the interaction between PLA and bitumen observed in the IR spectrum shown in Fig. 5. The washed (sequential dissolution) (WSD) and unwashed (PLA-modified bitumen) (UW) samples were compared to determine the inter-correlation between the existing functional group and the changes after blending. Based on the comparison of the washed and unwashed sam-

Table 3

Ductility and storage stability of base bitumen and PLA-modified bitumen.

Sample	Ductility at 25 °C (cm)	*Storage Stability			
		Top (°C)	Bottom (°C)	Difference (°C)	Status
Control Sample	>100	–	–	–	–
3% PLA	>100	50	51	1	Good
5% PLA	>100	58	60	2	Good
7% PLA	>100	59	61	2	Good
9% PLA	>100	68	72	4	Poor

\*difference between the softening point of the top and bottom sections

ples, it can be concluded that the interaction bond between asphaltenes and PLA is dependent on the carbonyl functionalities index. There is a different index pattern shown in addition to the band at region i (C-O) and region ii (C = O) when divided with C = C and C-C bonds (Fig. 5). Overall, the C = C bond decreases while the C-C bond remains unchanged in the UW samples of the control bitumen and the PLA modified bitumen. However, an increase in both the C = C and C-C bonds was observed in all WSD in comparison to the control bitumen. The increase in the amount of both alkenes and alkanes in the WSD is expected since both are a part of asphaltene, which is the product of sequential dissolution. The difference in the number of alkenes and alkanes in the UW indicates that one of them is probably involved in the chemical interaction between the bitumen and the PLA.

From the analysis of the C-O bond in region i, the 11.2% increase in the cumulative index of C-O with C = C relative to the control compared with the 2.5% decrease in that for C-O with C-C indicated the C-O bond formed in the PLA modified bitumen samples is related to the C = C interaction. This data is supported by the result of the WSD analysis, the index for C-O with C = C values remains unchanged (except for 9% PLA) while the C-O shows a decrease when divided with C-C area. The same index value for C-O with C-C in the WSD indicate that no C-O bond is detected in PLA because of its high compatibility with bitumen after the extraction process for sequential dissolution evaluation. Analysis of the carbonyl in region ii shows that the decrease in the carbonyl index of the WSD corresponds with the amount of asphaltenes dissolved in chloroform. The difference in the values of both carbonyl index between C = C (average, 15.1%) and C-C (average, 4.4%) in all PLA-modified bitumen samples is due to the significantly low C = C content in the samples after modification. Based on these values, it can be concluded that the interaction of bitumen with PLA is between C = C and not C-C. The result of NMR analysis (Fig. 4B) supports this conclusion since there is a suppression of signals at a chemical shift of between 1.5 and 3.5 ppm; these signals represent the alkene (C = C) group. Finally, the loss of OH group in region iii (Fig. 5) in the PLA-modified bitumen samples seems to indicate the following reaction mechanism between PLA and bitumen (Fig. 13).

Generally, all the supporting data from NMR and FT-IR suggest that the reaction between PLA and bitumen is an addition reaction. This reaction occurred when the hydroxyl group of PLA reacts with the alkenes in bitumen, where the formation of bridge C-O bonding found in the region based on FT-IR analysis. The finding is supported by the previous studies, indicating the certain chemical reactions between the functional groups of the components of the blends. This reaction or chemical compatibilization creates in-situ copolymers formation during processing [54,55]. This proposed mechanism is important since the structure of PLA has high compatibility with bitumen. The finding of new mechanism potentially provided the fundamental information related to the chemical interaction of PLA and bitumen which lead to the discovery of new modifiers that are better bitumen enhancer.

In addition to FT-IR analysis to determine the compatibility of PLA with bitumen, the dispersity of PLA throughout the base bitumen was also examined with Gel Permeation Chromatography (GPC). GPC was used to determine the molecular weight average of PLA modified bitumen. The profile of GPC varies between bitumen modified with 3, 5, 7 and 9% PLA relative to the control bitumen. It is worth noting that the peak eluted at ± 25.1 min, differentiates the bitumen from the bitumen-PLA samples. The molecular properties of this peak are presented in Table 2, and it shows a decline in the number of MP. The Mw, Mn and polydispersity index of the samples were compared to the control sample. Mn is the statistical average molecular weight of all PLA chains in the sample. Unlike Mn, Mw takes into account the molecular weight of a chain in determining its contributions to the average molecular weight.

Fig. 10 and Table 2 show that there is a significant difference in bitumen modified with 5% PLA (1456 gmol<sup>-1</sup>) and 7% PLA (2161 gmol<sup>-1</sup>). The heavier the chains have more contribution to Mw; therefore, a better PLA-bitumen interaction is observed with 7% PLA modification as compared to 3 and 5%. Polydispersity index is a measure of the distribution of PLA's molecular weight in the samples and is defined as Mw/Mn. The large polydispersity index indicates the broad distribution of molecular weight. The difference in polydispersity index of 5% (1.136) and 7% (1.653) PLA modification indicates that the bitumen showed the best chemical

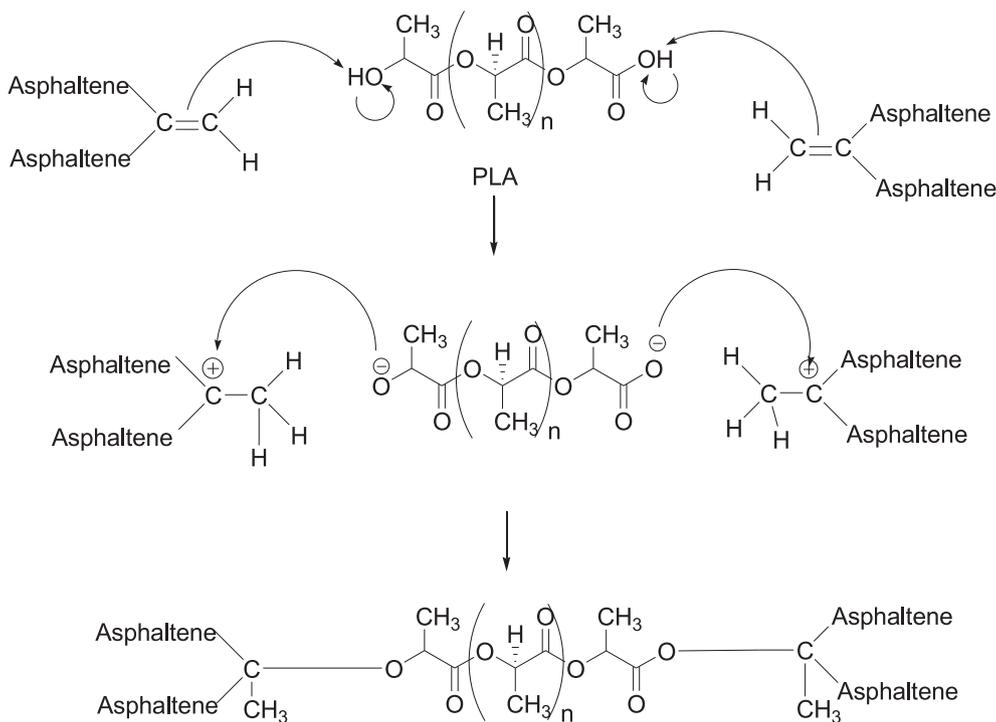


Fig. 13. Proposed reaction mechanism between PLA and bitumen.

interaction with the incorporation of up to 7% PLA. However, from the data of sequential dissolution, the 9% PLA showed a sequential dissolution effect resulting in reduced compatibility. In summary, based on the GPC and sequential dissolution data, the best modification of bitumen is achieved with 7% PLA. This result is supported by the characterization of the physical performance of PLA-modified bitumen. This research shows that the properties of modified bitumen with 7% of PLA is the good quality in terms of hardness, stiffness, ductility and storage stability ability. This is consistent with the previous discussion of the chemical interaction, compatibility and dispersity test.

## 6. Conclusions and suggestion for future study

This study aims to comprehensively evaluate the chemical and physical properties of PLA modified bitumen. The chemical properties were monitored using NMR, FTIR and GPC, while the physical properties of modified bitumen were measured by several empirical indexes in terms of penetration, softening point and ductility grading. Furthermore, the storage stability of the modified bitumen was also investigated in this study. The main conclusions of this research are:

- The addition of PLA into the base bitumen indicates the existence of chemical interaction between these materials. The findings of this study have shown the chemically cross-link at the alkene group (C = O) of PLA and hydroxyl group (OH) of bitumen.
- The results from GPC analysis shows high compatibility between the bitumen and PLA. The dispersion of PLA in the bitumen is found to be directly proportional with the amount of PLA, which results in the enhanced molecular properties of the PLA-modified bitumen.
- The physical properties of PLA modified bitumen obtained from the conventional bitumen tests show that the consistency of modified bitumen has increased as compared to the base bitumen with the low penetration and high softening point value. Also, ductility properties of modified bitumen indicate the permitted value as that of base bitumen.
- The modification of bitumen with up to 7% PLA is storage stable except for the modified bitumen with 9% of PLA content.
- In summary, the use of PLA in bitumen modification has a significant effect on the chemical and physical properties of modified bitumen. Based on the results, 7% PLA is recommended as the optimum amount for modifying base bitumen.

For future studies, a more comprehensive characterization of PLA modified bitumen for rheology properties can be carried out. There is a need to investigate the ageing of the PLA modified bitumen for the effect of oxidation and UV radiation on the rheological properties and the potential deterioration over time. Moreover, further research is recommended to investigate the application of PLA-modified bitumen in asphalt mixtures.

## 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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